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NBSIR 85-3280

Nylons: A Review of the Literature on Products of Combustion and Toxicity

ReferenceNBS
PUBLICATIONS

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February 1986

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U.S. Consumer Product Safety Commission
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NATIONAL BUREAU OF STANDARDS, Ernest Ambler, Director

TABLE OF CONTENTS

| | Page |
|--|------|
| LIST OF TABLES | iv |
| LIST OF FIGURES | vii |
| ABSTRACT | 1 |
| 1.0 INTRODUCTION | 2 |
| 2.0 CHEMICAL STRUCTURE AND THERMOPHYSICAL PROPERTIES | 4 |
| 3.0 DECOMPOSITION | 5 |
| 3.1 VACUUM PYROLYSIS | 7 |
| 3.2 DECOMPOSITION IN INERT AND AIR ATMOSPHERES | 8 |
| 3.2.1 GENERAL DECOMPOSITION PRODUCTS | 8 |
| 3.2.2 SPECIFIC GAS SPECIES | 11 |
| 3.2.2.1 PURE MATERIALS | 11 |
| 3.2.2.2 COMPOSITE MATERIALS | 14 |
| 4.0 TOXICITY | 17 |
| 4.1 DIN 53 436 | 19 |
| 4.2 FAA TOXICITY PROTOCOL | 20 |
| 4.3 NASA/USF TOXICITY PROTOCOL | 22 |
| 4.5 MISCELLANEOUS | 27 |
| 5.0 LARGE-SCALE TESTS | 31 |
| 6.0 CONCLUSIONS | 35 |
| 7.0 ACKNOWLEDGEMENTS | 36 |
| 8.0 REFERENCES | 37 |

LIST OF TABLES

| | Page |
|---|------|
| TABLE 1. Thermophysical Properties of Nylons | 43 |
| TABLE 2. Mass Spectrometric Analyses of Gaseous Fractions From the Pyrolysis of Polyamide Copolymers | 44 |
| TABLE 3. Hydrocarbons Detected in the Pyrolysate of Polyamide Copolymers | 45 |
| TABLE 4. Mass Spectrometric Analysis of Volatile Fractions From the Pyrolysis of Various Polyamides | 46 |
| TABLE 5. Pyrolysis Products of Four Polyamides Determined by Gas Chromatography/Mass Spectrometry | 47 |
| TABLE 6. Thermooxidation Products of Four Polyamides Determined by Gas Chromatography/Mass Spectrometry | 48 |
| TABLE 7. Combustion Products of Nylons Decomposed in Different Oxygen Concentrations | 50 |
| TABLE 8. Combustion Products Generated by Decomposing Nylon 6 and Nylon 6,6 in a TGA in Air at 370°C | 51 |
| TABLE 9. Analysis of Cup Furnace Decomposition of Flaming Nylon 6,6 in Air | 52 |
| TABLE 10. Production of HCN and CO during Flaming Degradation of Nylon 6,6 in a Tube Furnace in an Air or Nitrogen Atmosphere | 53 |
| TABLE 11. Production of NO ₂ From the Thermal Degradation of Nylon 6,6 | 54 |
| TABLE 12. Concentration of Selected Products from the Thermal Decomposition of Nylon 6 in Air | 55 |
| TABLE 13. HCN Production From the Thermal Degradation of Three Nylons in Nitrogen or Air Atmospheres | 56 |
| TABLE 14. Concentrations of Specific Combustion Products Found During NBS Smoke Chamber Tests of Materials Containing Nylon | 57 |
| TABLE 15. Comparison of Colorimetric Detector Tubes and Instrumental Methods for Analyzing Gases Generated from the Thermal Decomposition of Two Flame Retarded 90% Wool, 10% Nylon Upholstery Fabrics in the NBS Smoke Chamber | 58 |

LIST OF TABLES (continued)

| | Page |
|--|------|
| TABLE 16. Comparison of Combustion Products Generated by a Combustion Tube Furnace From Two Flame Retarded 90% Wool, 10% Nylon Upholstery Fabrics | 59 |
| TABLE 17. Thermal Decomposition of Three Nylon Carpet Samples in an Infrared Pyrolysis Instrument | 60 |
| TABLE 18. Summary of Toxicity Protocols | 61 |
| TABLE 19. DIN Toxicity Test Results of a Treated and Non-Treated 85% Wool, 15% Nylon Carpet with a Jute Back | 62 |
| TABLE 20. Description of Nylon Containing Materials Evaluated by FAA Toxicity Test Method | 63 |
| TABLE 21. Incapacitation and Lethality Results from Exposures to Thermal Degradation Products from Nylon-Containing Materials Decomposed According to the FAA Protocol | 64 |
| TABLE 22. Effects of Backcoating on the Toxicity of a Nylon 6,6 Fabric | 65 |
| TABLE 23. Effects of Acid Dyes on the Toxicity of a Nylon 6,6 Fabric | 66 |
| TABLE 24. Effects of Various Heating and Airflow Conditions on the Toxicity of the Pyrolysis Products from Upholstery Fabrics Containing Nylon | 67 |
| TABLE 25. NASA/USF Toxicity Protocol B Results for a Series of Nylon Containing Fabrics | 68 |
| TABLE 26. Mean Times to Death and Incapacitation for Some Nylon Containing Materials Tested According to NASA/USF Toxicity Protocol B | 69 |
| TABLE 27. Comparison of Dynamic and Static Exposures for Nylon Materials | 70 |
| TABLE 28. Results of Animal Exposures to the Combustion Products of Nylon 6,6 Generated at Three Different Temperatures | 71 |
| TABLE 29. Results of Animal Exposures to Nylon 6,6 Decomposition Products Produced at 550°C and 850°C | 72 |
| TABLE 30. Gas Analysis of Large-Scale Tests of Innerspring Mattresses and Upholstered Chairs | 73 |

LIST OF TABLES (continued)

| | Page |
|---|------|
| TABLE 31. Large-Scale Nylon Carpet Tests Using NBS Corridor Facilities | 74 |
| TABLE 32. Results of Gas Analysis for Large-Scale Tests of Nylon Carpet and Various Underlayment | 75 |
| Table 33. Results of Large-Scale Tests of a Fully Furnished Burn Room Connected to a Corridor and Target Room | 76 |

LIST OF FIGURES

| | Page |
|---|------|
| FIGURE 1. The Production of Specific Gases from the Decomposition of Nylon 6 in an Atmosphere of Nitrogen | 77 |
| FIGURE 2. The Production of Specific Gases from the Decomposition of Nylon 6 in an Atmosphere of Air | 78 |
| FIGURE 3. Comparison of HCN and NH ₃ Production from the Decomposition of Nylon 6 in a Nitrogen Atmosphere | 79 |
| FIGURE 4. Production of HCN During Decomposition of Nylon 6 | 80 |

NYLONS: A REVIEW OF THE LITERATURE ON PRODUCTS
OF COMBUSTION TOXICITY

Emil Braun
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ABSTRACT

The literature on polyamides was reviewed to determine the nature and extent of information available on these materials which are commonly used in consumer and industrial applications. This review was limited to aliphatic polyamides normally called nylon and excludes aromatic polyamides such as Nomex and bicomponent polymers consisting of nylon and other polymers. The review was further limited to those publications in English through June 1984.

Typical pyrolysis products from a broad range of nylons do not appear to differ greatly. Many of the decomposition products detected in vacuum pyrolysis experiments appear as products of thermal degradation in inert and air atmospheres. In air, a general reduction in the quantities of heavier hydrocarbons is noted along with an increase in the production of CO, CO₂, H₂O, NH₃, HCN, and NO_x.

The toxicity of the thermal degradation products from various types of nylon has been evaluated by nine different protocols. Reported LC₅₀ values range from 10.8 mg/l to 61.9 mg/l. Dyes apparently do not affect the materials' combustion products toxicity, but an increase in the amount of backcoating on a nylon fabric increases toxicity. Time to death measurements

show that volatile products from nylons are less toxic than those from rayons or cotton, while the blending of wool with nylon greatly increases the toxicity of the thermal decomposition products. In general, however, the overall toxicity of the thermal degradation products from nylon do not appear to be greatly different than those from many other polymeric materials.

Large-scale test results are ambiguous, and it is difficult to interpret the results in terms of a single component in a multicomponent system.

Keywords: Combustion products; literature reviews; nylon; pyrolysis, thermal decomposition; toxicity.

1.0 INTRODUCTION

It is generally agreed that the quantity of smoke produced and its toxicity play an important role in determining the likelihood of surviving a building fire. Researchers over the past two decades have become increasingly concerned with the measurement of toxic effects from burning materials under a great many combustion conditions. Recently, many laboratories have attempted to develop standard laboratory-scale toxicity protocols. In the wake of this research and testing, much information has been scattered throughout the technical literature on a great many materials. In an effort to collect, compare, and systematize this information, the fire toxicology group within the Center for Fire Research at the National Bureau of Standards conducted a literature review on several classes of synthetic materials.

In this report, the literature on polyamides is reviewed to determine the nature and extent of information available on these materials which are commonly used in consumer applications, such as wearing apparel and interior furnishings, and industrial applications (e.g., belts, filters, and molded components). This review is limited to aliphatic polyamides normally called nylon and excludes aromatic polyamides such as Nomex¹ and bicomponent polymers consisting of nylon and other polymers. The review is further limited to those publications in English through June 1984. A total of 10 databases (Chemical Abstracts, Environmental Abstracts, Excerptica Medica, FRIS Library, Medline, NTIS, RAPRA, RTECS, TRIS, and Toxline) were searched for pertinent publications.

The primary purpose of this review was to determine the possible products of combustion that aliphatic polyamides would yield under various fire conditions and to evaluate the toxicity of these products of combustion. In general, fire investigators, either combustion scientists or toxicologists, do not specifically identify the exact formulation of nylon used in their respective studies. This severely limits the validity of any comparison of results between different investigators. Differences in experimental procedures may be overshadowed by the use of different nylons. Nevertheless, a range of values can be obtained that are descriptive of the

¹ Certain commercial equipment, instruments, or materials are identified in this paper in order to adequately specify the experimental procedure. In no case does such identification imply recommendation or endorsement by the National Bureau of Standards, nor does it imply that the equipment or material identified is necessarily the best available for the purpose.

class of materials called nylon. This includes thermophysical properties as well as products of combustion and, therefore, toxicity.

2.0 CHEMICAL STRUCTURE AND THERMOPHYSICAL PROPERTIES

Nylon is a generic name referring to a series of aliphatic polyamides. These polymers contain the recurring amide group, -CONH-. The usual method for describing a particular type of nylon is by attaching a number designation to the word nylon that represents the number of carbons in the repeating units of the raw stock. For example, nylon 6,6 is made from hexamethylene-diamine and adipic acid - each containing 6 carbons. There are four methods available for the production of nylon: 1) hydrolytic polymerization; 2) anionic polymerization; 3) interfacial polymerization; and 4) solid-state polymerization. Of these, hydrolytic polymerization is the most common [1]². Nylons may be formed by either polycondensation of a diamine and a dibasic acid, as in the case of nylon 6,6, or polymerization of a caprolactam or amino acid as in the case of nylon 6. Nylons can be formed into fibers, films, or cast into molded end products which are either reinforced or unreinforced.

The thermophysical properties of nylons can vary depending on formulation. Table 1 summarizes the range of values found during this review. Nylons have a melting point that ranges from approximately 172 to 260°C [1,2]. Nylon 12 had the lowest melting point temperature, while nylon 6,6

² Numbers in brackets refer to the literature references listed at the end of this review.

had the highest reported value. Nylon 6 was found to be in the 215 to 220°C range [2]. Ignition temperatures were also found to vary from 421 to 590°C for flash ignition [3,4,5,6,8] and 424 to 532°C for self-ignition [4,8]. These values also varied according to nylon type. Nylon 6,6 had the highest values, while nylon 6 had mid-range values. The lowest values were reported for a set of undefined nylons.

Jellinek [6] determined that the thermal decomposition activation energy for nylon 6,6 was 223 kJ/mole. Reardon and Baker [7] reported a value of approximately 180 kJ/mole for nylon 6.

Hilado [8] reported Oxygen Index values for various nylons ranging from 20.1 to 28.7. The higher values represented undefined nylons that may contain flame retardant compounds.

3.0 DECOMPOSITION

The thermal decomposition of nylons has been shown to begin with a primary scission reaction of an $-\text{NH}\cdot\text{CH}_2-$ bond followed by a complex series of secondary reactions [11,12]. Subsequent intermediate mechanisms of decomposition depend upon the specific structure of the nylon, but combustion end products do not differ greatly among the nylons studied. Some reaction schemes require the presence of free radicals, as in the case of nylon 6 [11], while other schemes require the production of water which later leads to hydrolysis of polymer fragments [12]. Strauss and Wall [13] studied various nylons and concluded that decomposition was caused by free radical

formation and random scission. The primary site for scission was the C-N bond. Conway and Marak [14] postulated that in the pyrolysis of nylon 6,6, substituted cyclopentanone groups are formed by NH-CO bond scission and ring closure. Large quantities of carbon dioxide (CO_2) and ammonia (NH_3) would be expected along with n-hexylamine. These were detected by chemical ionization mass spectrometry when nylon 6,6 was pyrolyzed directly into the ion source of a mass spectrometer (MS).

The experimental work on thermal reactions of this type has been done either in vacuum or in inert gas atmospheres. This research has been aimed at deducing the chemical mechanisms and energies involved in each reaction step. Studies under normal atmospheric conditions of 21% oxygen (O_2) are limited to describing the nature of the combustion products.

In the next few sections of this report, we will describe the gaseous products that evolved during thermal decomposition in each of three environments - vacuum, inert atmospheres, and air. While it may not appear relevant to the real fire situation to review work done under oxygen-free conditions, it must be realized that studies such as these provide information about the effects of well controlled conditions on the nature and amounts of volatile products of thermal decomposition. As will be seen, some of these volatile products survive the passage through or past the flame and appear ultimately as products of incomplete combustion during atmospheric burning of the polymer.

3.1 VACUUM PYROLYSIS

Achhammer et al. [12] used a mass spectrometer to analyze the gases generated when nylon was heated to 400°C for 30 minutes in a vacuum. Two nylon copolymer samples were used. One was a copolymer of nylon 6,6 and nylon 6, while the other was a copolymer of nylon 6,6 and nylon 6,10. Approximately 5% of the original weight of a sample was converted to gaseous fractions. Table 2 summarizes these results. The copolymer of nylon 6,10 produced no carbon monoxide (CO) and very little water. This is in contrast to the nylon 6 results which produced significant amounts of water and CO. Table 3 is a tabulation of the hydrocarbons detected by Achhammer et al. [12] from the copolymers of Table 2.

Strauss and Wall [13] pyrolyzed various nylon polymers in a vacuum oven at 400°C for 30 minutes. Table 4 compares the pyrolysis products of a nylon 6 and nylon 6,6 copolymer similar to one of the copolymers studied by Achhammer et al. [12] with the pyrolysis products of two types of nylon 6, differing in molecular weight, and a nylon 6,10. For these samples tested, carbon dioxide and water represented 80-95% of the total volatiles detected. A large number of simple hydrocarbons was identified. Cyclopentanone was only detected with the copolymer.

Peebles and Huffman [15] heated nylon 6,6 at 305°C under vacuum and found that the major volatiles were CO₂, NH₃, and H₂O. In addition, they

also detected cyclopentanone, 2-cyclopentylidinocyclopentanone, 2-cyclopentylcyclopentanone, hexylamine, hexamethyleneimine, hexamethylenediamine, and 1,2,3,5,6,7-hexahydrodicyclopenta[b,e]pyridine.

3.2 DECOMPOSITION IN INERT AND AIR ATMOSPHERES

Investigations into the decomposition products of aliphatic polyamides in inert atmospheres and air can be divided into two general categories. Several researchers have studied the broad range of decomposition products produced by the thermal degradation of polyamides, while other researchers have concentrated on the parameters affecting the production of specific chemical species. The chemical species usually investigated have been NH₃, hydrogen cyanide (HCN), and oxides of nitrogen (NO_x) along with CO, CO₂, and water.

3.2.1 GENERAL DECOMPOSITION PRODUCTS

Senoo et al. [16] used pyrolysis/gas chromatography with a nitrogen carrier to analyze the degradation products from a copolymer of nylon 6 and nylon 6,6. By varying the pyrolysis temperature from 400 to 840°C, they were able to determine that cyclopentanone and ϵ -caprolactam first appeared at 480°C. The production of cyclopentanone was temperature dependent and went through a minimum around 550°C. The low boiling point gases detected were: acetonitrile, acrylonitrile, benzene, hexamethylenediamine, pyridine, pyrrole, and styrene.

Michal et al. [17] used Curie point heating to decompose four polyamides cast on ferromagnetic wires. They analyzed the decomposition products produced at three temperatures, 510, 610, and 770°C, using a gas chromatography/mass spectrometry (GC/MS) system (Table 5). They did not analyze for CO, CO₂, or water, but concentrated on characterizing hydrocarbons with a carbon chain of greater than five. They found that the production of nitrile compounds depended on both the temperature and formulation of the polyamide. Nylon 11 produced nitrile compounds at all three temperatures. The first nitrile compound produced by nylon 6 was acetonitrile at 770°C. As the carbon length of nylon was decreased, higher temperatures were required to produce nitrile compounds.

Michal et al. [17] continued their investigations into the decomposition of these materials by conducting thermogravimetric analysis (TGA) experiments with laboratory air flowing through the system. The samples were heated at 15°C/min over the temperature range of 200 to 700°C. Initial sample weight was 5 mg. The analysis of the combustion products was conducted by GC/MS. Table 6 is a list of the combustion products reported for all four polyamides. In comparing the results of Tables 5 and 6, it should be noted that, under conditions of nitrogen pyrolysis, nylons 7, 8, and 11 produced cyclopentanone when heated above 600°C, while nylon 6 did not produce any cyclopentanone at any temperature. However, in an air environment, nylon 6 produced cyclopentanone, while the other polymers did not.

Dufour [18] cites the unpublished work of Hobbs and Patten who used Vycor combustion tubes heated in a tube furnace to 800°C. "Free burning"

tests were conducted with laboratory air (20.9% O₂), while smoldering tests employed a mixture of nitrogen and oxygen (11.7% O₂). While the specific type of nylon was not defined, Table 7 indicates that as the oxygen concentration increased, the production of CO₂ increased and the production of other gas constituents decreased. They did not measure the production of H₂O or NO_x which would be expected to increase with increasing oxygen.

Using similar equipment, Hartstein and Forshey [19] determined the combustion products of nylon 6, while Christos et al. [20] evaluated the combustion products of nylon 6,6. They decomposed these polymers in air at 370°C, and measured the components of the effluent gas stream using a TGE apparatus coupled to a GC/MS system (Table 8). Both polymers produced similar gas constituents, but at different concentrations. The nylon 6 results reported by Hartstein are consistent with the nylon 6 results of Michal et al. [17] as shown in Table 6.

Morimoto et al. [21] decomposed 0.1 g samples of nylon 6,6 in a cup furnace at 700°C with an airflow of either 50 l/h or 100 l/h (Table 9). In addition, the data tabulated in Table 9 were determined by infrared spectrophotometry. Increasing the airflow rate increased the concentration of all of the decomposition products. They found that during flaming combustion, 69% of the nitrogen contained in the polymer was converted to N₂. Small amounts of NO and NO₂ were also detected - 0.3 mg/g and 0.07 mg/g, respectively. However, they did not specify the flow conditions under which the NO_x measurements were made.

3.2.2 SPECIFIC GAS SPECIES

Since nylon contains nitrogen in its chemical structure, some researchers have directed their efforts at measuring nitrogen-containing gaseous species produced during thermal decomposition. In general, emphasis has been placed on monitoring the production of HCN, NH₃, and NO_x to the exclusion of other combustion products.

3.2.2.1 PURE MATERIALS

Dufour [18] references the unpublished work of McDermott and Critchfield who measured the amount of HCN produced by pyrolyzing nylon (type not specified) in a one liter round bottom flask. They placed a 20 mg sample of nylon in the flask and heated it with a Terrill burner for 60 seconds. When the flask was initially filled with nitrogen, they measured 280 $\mu\text{g/g}$ of HCN. This increased to 780 $\mu\text{g/g}$ in a subsequent experiment when the flask was filled with air.

Using a Differential Thermal Analysis (DTA)-GC/MS system, Murata and Takahashi [22] were able to determine that nylon 6, heated at 10°C/min in an air atmosphere, began producing HCN and NH₃ at about 375°C.

Bott et al. [23] used a tube furnace to decompose a nylon sample (type not specified) in air and nitrogen atmospheres. With a flow rate of 250 mL/min of air, they reported a temperature of 350°C for the initial evolution of HCN and NH₃. Carbon monoxide also began evolving at this temperature.

The presence of NO_x was first detected at 600°C. In a nitrogen atmosphere, similar experiments showed that CO and NH_3 were initially liberated at 300°C. At 350°C, HCN was detected, while NO_x appeared at 650°C. Using 1 g samples, they reported that the percent by weight of HCN produced by heating nylon in air and in nitrogen was 0.04% and 0.03%, respectively. At a fixed temperature of 500°C, they measured the following gas concentrations:

| <u>Gas</u> | <u>Concentration in</u> | |
|---------------|-------------------------|--------------------------|
| | <u>Air</u> (ppm) | <u>Nitrogen</u> (ppm) |
| HCN | 200 | 80 |
| CO | 1200 | 600 |
| NH_3 | 20000 | 10000 |

Mapperley and Sewell [24] also used a tube furnace to measure the production of HCN and CO from the thermal decomposition of nylon 6,6 in either air or nitrogen atmospheres. With a gas flow of 50 ml/min, 10 mg samples were placed in the furnace. Decomposition was conducted at fixed temperatures within the range of 700 to 1100°C. Their results indicate that the production of CO increased with increasing temperature and was higher for an air atmosphere than for an nitrogen atmosphere at temperatures above 900°C (Table 10). The HCN yield was not significantly affected by the combustion atmosphere, and appeared to have a maximum yield between 900°C and 1000°C.

Skidmore and Sewell [25] repeated the work of Mapperley and Sewell [24] but added NO_x measurements. Using colorimetric detector tubes³ and an airflow rate of 500 ml/min through the tube furnace, they found that NO_x (reported as NO_2) production decreased as the temperature increased from 600 to 800°C and then increased as the temperature increased from 800 to 1000°C (Table 11). At 1000°C, they found that considerably less NO_x (0.94% of the sample weight) was produced than HCN (11.6% of the sample weight). Approximately 54% of the available nitrogen was converted to HCN, while only 2.3% appeared as NO_x .

Sugihara [26], Sumi and Tsuchiya [27], and Morikawa [28] employed tube furnaces to thermally degrade nylon 6 over the temperature range of 400 to 1000°C in air or in nitrogen atmospheres. Sugihara [26] monitored the production of HCN, CO, NH_3 , and NO_2 , while Sumi and Tsuchiya [27] monitored HCN, CO, and CO_2 . Morikawa was concerned with the production of NH_3 and HCN. All three found that the production of HCN increased with increasing temperature in either air or nitrogen atmospheres. Sugihara reported that the production of CO in air or in nitrogen increased with temperature, while Sumi noted that it was relatively independent of temperature. Sugihara's data for CO, CN^- , and NH_3 are summarized in Figures 1 and 2, while Figure 3 shows the results of Morikawa's work comparing the production of HCN and NH_3 as a function of temperature in a nitrogen atmosphere. Figure 4 shows Morikawa's results for HCN production in air and nitrogen atmospheres. Sumi's results are tabulated in Table 12.

³ See ASTM E 800, Standard Guide for Measurement of Gases Present or Generated During Fires, for cautionary notes on the use of gas detector tubes [63].

Using a commercial oven with a 15 in³ cavity, Rigby [29] determined that NH₃ was the major decomposition product when nylon 6, nylon 6,6, and nylon 11 were heated at 250°C in air. The concentrations of NH₃ produced by the three nylon samples were:

| <u>Material</u> | <u>NH₃</u> (ppm/m ³) |
|-----------------|--|
| nylon 6 | 2.9 |
| nylon 6,6 | 4.3 |
| nylon 11 | 2.9 |

Michal [30] compared the HCN production of three nylons when thermally decomposed in a tube furnace between 600°C and 1200°C with air or nitrogen flowing at 50 ml/min (Table 13). He found that, in all three cases, the HCN concentration increased with increasing temperature and was independent of combustion atmosphere. In general, from 600 to 1000°C, nylon 6,6 produced a higher concentration of HCN than nylon 11 or nylon 12. At 1200°C, nylon 11 produced a little more HCN than nylon 6,6 or nylon 12.

3.2.2.2 COMPOSITE MATERIALS

In general, combustion tube experiments are not well suited for the analysis of combustion products from composite materials; the primary problem being the testing of representative portions of the composite material. For this reason, several researchers have adapted the NBS Smoke Chamber [65] to

generate combustion products from a wide range of composite materials. These combustion products are then analyzed employing many of the same techniques used in combustion tube experiments.

One of the earliest attempts at characterizing combustion products produced by composite materials in the NBS Smoke Chamber was done by Gross et al. [31]. They used colorimetric or gas detector tubes in an effort to measure the amounts of specific low molecular weight compounds found in the chamber's atmosphere. They tested a total of 141 aircraft interior materials, eleven of which contained nylon. A description of the nylon containing materials and concentrations of specific gases reported in terms of the mass of material tested are presented in Table 14. It is interesting to note that, except for two materials, HCN was detected in all samples under both flaming and non-flaming conditions. Also, in the majority of samples, the flaming condition produced higher concentrations of CO, HC_l, and HCN.

In a similar set of experiments, Speital et al. [32] decomposed composite materials in the flaming mode in an NBS Smoke Chamber and measured the presence and concentrations of low molecular weight compounds in the combustion gases. They compared colorimetric detector tubes with instrumental methods of analysis. Two fire retarded upholstery fabrics, both containing 90% wool and 10% nylon, were tested. The results were reported in terms of mass of gas per mass of consumed material (Table 15). These findings are in contrast to those of Gross et al. [31] who reported their results in terms of material initially placed in the smoke chamber. It can be seen that no pattern appears. For SO₂ and NO₂, the colorimetric detector

tubes greatly overestimate the presence of these gases in comparison to the instrumental methods, while the colorimetric detector tubes underestimated the concentration of H₂S. The data also show inconsistent results for CO and HCN.

Speital et al. [32] also designed and built a combustion tube furnace capable of holding 250 mg samples. They heated the previous two wool/nylon samples for 5 minutes at 600°C with an ambient airflow rate of 2 l/min. The combustion gases were analyzed by a set of instrumental methods similar to those previously cited (Table 16). Comparing Table 16 and Table 15, it can be seen that these combustion tube experiments yielded higher concentrations of HCN and CO than the NBS Smoke Chamber tests.

Melvin [33] decomposed 10-30 mg samples from three nylon carpets in an infrared pyrolysis instrument in the temperature range of 400 to 650°C. Table 17 contains a description of the carpet samples and the test results. The reported results are normalized to a one square foot of carpet per cubic meter of air. As expected, the specimen containing PVC also produced HCl.

While the exact products of decomposition depend on the specific nylon used, several generalizations can be made regarding the effects of atmosphere and temperature on the decomposition of these polymers. Vacuum decomposition of nylons, at 300 to 400°C, produced large quantities of CO₂ and H₂O. In some cases, NH₃ was detected in significant amounts. Many of the same compounds detected under vacuum conditions of decomposition were also produced during heating under inert or air atmospheres. Several researchers

have shown that HCN, NH₃, and NO_x were produced during thermal degradation in both inert and air atmospheres. Due to heat losses to the furnace walls, the design of some combustion systems may prevent flaming combustion from actually occurring, although decomposition had taken place in an air atmosphere with a sufficiently high temperature to cause flaming under other experimental conditions.

4.0 TOXICITY

At least nine different protocols have been used to assess the toxicity of the thermal degradation products of nylon materials. These protocols are briefly summarized in Table 18, and can be divided into two classes. The first class (no. 1-4) of protocols represent widely recognized procedures for evaluating combustion product toxicity. These procedures were developed for the purpose of providing information on a broad range of materials. The second group of protocols (no. 5-9) were developed on an ad hoc basis to evaluate the combustion product toxicity of selected materials. It appears that the researchers in the second group did not intend to design a general purpose test protocol that could be used for material toxicity evaluations. Those protocols marked with an asterisk in Table 18 are described in greater detail by Kaplan et al. [34]. Additional citations that provide for a more complete description of each test protocol will be given as each method is discussed in the following sections.

Toxicologists have developed numerous terms for describing a material's toxicological potency. Combustion toxicologists have used either incapacitation or lethality endpoints as characteristic indices of a material's toxicity. These values are reported for a given exposure concentration as the time to effect or the percent of affected animals within a fixed exposure time. In combustion experiments, the exposure concentration is a measure of the amount of combustion products present in the exposure atmosphere based on the material placed in a combustion apparatus or the fraction actually decomposed. The biological endpoint most often used by combustion toxicologists has been that concentration of combustion products affecting 50% of the exposed animals. Therefore, terms such as LC_{50} , LL_{50} , LA_{50} , and $L(Ct)_{50}$ refer to a lethal amount of combustion products which affect 50% of the exposed animals.

An LC_{50} is the lethal concentration reported in terms of mass of material loaded or consumed in the furnace per unit volume of the exposure chamber (e.g., mg/l). Some researchers have misused this nomenclature by assigning to it units of mass only. In this report, LL_{50} , lethal loading, is employed to indicate mass (e.g., gm) which has not been normalized by volume. The LA_{50} , lethal area (e.g., cm^2), is a description of the initial surface area of exposed sample that produced the combustion atmosphere which caused death in 50 percent of the animals. The $L(Ct)_{50}$, whose dimensionality is typically ppm-min, is determined by calculating the area under the concentration-time curve generated for a particular gas during the decomposition of a material.

4.1 DIN 53 436 METHOD

The DIN 53 436 test method was developed in the Federal Republic of Germany. It provides a steady output of combustion products and uses a horizontal moving tube furnace to decompose the sample in a flowing air stream [35]. The combustion air stream is diluted with room air and then introduced into an animal exposure chamber. The combustion products flow past the animals and are exhausted out of the system. Material is introduced into the combustion system based on equal specimen volume or weight per unit length.

Herpol [36] exposed three male and three female rats per test to the combustion products generated by two carpet samples composed of 85% wool and 15% nylon and backed with jute. One carpet sample was treated with K_2ZrF_6 . All of the tests were conducted for 30 minutes with combustion air flowing at 200 l/hr. Tests were conducted at 500, 600, and 700°C (Table 19). The treated carpet sample flamed at all three temperatures, while the non-treated sample did not flame at 500°C, but did flame at 600 and 700°C. As the temperature increased above 500°C, CO production decreased for both samples; CO₂ production increased for the non-treated sample and remained relatively constant for the treated sample. This was as expected since the treated sample flamed at all three test temperatures. At a given temperature, the mean respiration frequencies (percent of normal pre-exposure value) were lower for those animals exposed to the combustion products from the treated sample than the non-treated sample. For those tests that had animal deaths, (500°C for the non-treated sample and 500 and 600°C for the treated sample)

the mean carboxyhemoglobin (COHb) was found to be 37% in those animals exposed to the decomposition products from the non-treated sample and 60% and 25%, respectively, from the treated sample. Herpol [36] found that preliminary experiments with CO showed that deaths would first occur when the CO concentration was 4000 ppm, resulting in COHb levels of 65%. Except for the treated sample tested at 500°C, all other values were well below this CO exposure level and corresponding COHb levels were below the critical value of 65%. Therefore, in these experiments, death can be considered to be caused by the presence of combustion products in the gas stream in addition to CO.

4.2 FAA TOXICITY PROTOCOL

Crane et al. [37], at the Federal Aviation Administration (FAA), have developed a small-animal inhalation toxicity system in which the system atmosphere is recirculated between a tube furnace set at 600°C and an animal exposure chamber. In each experiment, three albino rats are exposed for a maximum of 30 minutes in a whole body mode. The biological endpoints are time to incapacitation, as determined by the animals' inability to move in an exercise wheel, and time to death. The samples tested were commercially available aircraft interior materials. Sample mass was fixed at 750 mg, which would be equivalent to a concentration of 60 mg/l if completely consumed. Crane et al. reported three sets of time values. One set was the actual time to effect, while the other two were values normalized to a 200 gram animal and a sample weight of 1 gram (sample weight was either that charged to the system or that consumed during the test). Data based on charged weight was called "standard" and that based on consumed weight was

called "loss." Of the 75 materials tested by Crane et al., three contained nylon. Their descriptions are listed in Table 20 and the test results are presented in Table 21. Sample 142, a flame retarded wool/nylon upholstery fabric was the most toxic, while sample 89, a flame retarded PVC/nylon fabric, was the least toxic. In fact, sample 89 produced no animal deaths during exposure. Normalizing the data as described above does not change the toxic order of the materials.

Fewell et al. [39] used the same protocol to evaluate the toxicity of a flame retarded treated nylon fabric and found that the time to incapacitation was 2.89 minutes and the time to death was 4.00 minutes (values were normalized to a 200 g rat and 1 gram of sample). Speith and Trabold [38] compared the results of Fewell et al. to a 90% wool and 10% nylon upholstery fabric. In both cases, the combustion tube furnace was also set at 600°C and the total exposure time was 30 minutes. The first 200 seconds involved the active decomposition of the sample. Reporting their results in terms of a value normalized to 1 g of material per 25 g of animal body weight, they found that the blended fabric was more toxic than the 100% nylon.

| Fabric | Loading (mg/ℓ) | Mean Time ^a to | |
|------------------|-------------------|---------------------------|----------------|
| | | Incapacitation (min) | Death (min) |
| 100% nylon | 86 | 2.89±0.93 ^b | 4.00±0.61 |
| 90%wool/10%nylon | 35 | 0.83±0.18 | 2.59±1.66 |

^a normalized to 1 g of material and 25 g of animal body weight.

^b standard deviation.

4.3 NASA/USF TOXICITY PROTOCOL

The NASA/USF Toxicity Protocol was developed for the National Aeronautical and Space Administration (NASA) and used extensively by Hilado at the University of San Francisco (USF). This method exposes four Swiss-Webster male mice to the combustion products developed in a horizontal tube furnace. The animals are allowed to move freely in a 4.2 liter animal exposure chamber. The exposure chamber is connected to the furnace by a glass tube. The furnace can be operated at fixed temperatures or ramped at a rate of 40°C/min from 200 to 800°C. Movement of the combustion products is due to thermal expansion except under a modified test protocol using flow-through conditions when a pump is used to move air through the system at 3 l/min. Because of the nature of the apparatus and the use of incapacitation time as the figure of merit, results from this method are highly sensitive to the thermal stability of the polymer being tested.

Young et al. [40] used this method to characterize generic polymers. They ramped the furnace at 40°C/min until 700°C at which temperature the furnace was maintained for 30 minutes. The total exposure time was, therefore, 47.5 minutes. Specific gases were detected by colorimetric detector tubes. For a polyamide, they found an LC₅₀ of 32 mg/l along with a CO concentration of 2000 ppm and a CN⁻ concentration of 1000 ppm.

Kourtides et al. [41] evaluated the combustion product toxicity of three types of nylons and reported the mean times to death and the mean times to

incapacitation where the means are calculated from the average values obtained from at least three tests. They decomposed one gram samples by ramped heating at 40°C/min. The results are shown below.

| <u>Material</u> | <u>Mean Time (min) To</u> | |
|-----------------|---------------------------|-----------------------|
| | <u>Death</u> | <u>Incapacitation</u> |
| nylon 6,10 | 13.28 ± 1.63^a | 11.48 ± 1.59 |
| nylon 6 | 13.47 ± 1.13 | 11.55 ± 0.66 |
| nylon 6,6 | 16.34 ± 0.85 | 14.01 ± 0.13 |

^a standard deviation of results of at least three tests.

In addition, they determined an apparent lethal concentration, ALC_{50} , of 10.75 mg/l for a 30 minute exposure to the decomposition products of nylon 6.

Hilado and Huttlinger [42] repeated this work for nylon 6. They reported a mean time to death of 21.04 ± 2.78 minutes. In another report, Hilado [43] reported CO and CH_4 measurements of 5480 ppm and 1970 ppm, respectively, from the decomposition of this material. Using two different sources of nylon 6,6 and two different sources of nylon 6,10, Hilado and Cumming [44] found the following results for the mean times to death:

| <u>Sample</u> | <u>Mean Time to Death (min)</u> | |
|---------------|---------------------------------|-------------------|
| | <u>nylon 6,6</u> | <u>nylon 6,10</u> |
| A | 18.15 | 15.48 |
| B | 16.20 | 13.47 |

They also measured the CO and CO₂ concentrations at the end of each test and found that for nylon 6,6, the CO concentration was 9300 ppm and 13000 ppm for samples A and B, respectively. The comparable results for nylon 6,10 were 11560 ppm and 14260 ppm. The CO₂ results varied from 3.5% to 4.5%.

Hilado and Huttlinger [45], Hilado et al. [46], Hilado and Brauer [47], and Hilado and Huttlinger [48] investigated the effects of dye and backcoating on the toxicity of the pyrolysis products of a nylon fabric exposed to ramped heating of 40°C/min. The results in Table 22 indicate that dyes do not appear to affect the toxicity of nylon, however, an increase in the amount of backcoating applied to the nylon fabric decreased the mean times to death (Table 23).

Table 24 is a tabulation of the mean times to incapacitation and times to death for two upholstery fabrics exposed to seven different combinations of heating and airflow test conditions. In general, the 100% nylon fabric appeared to be substantially less toxic than the 86% wool/14% nylon fabric.

Hilado and Brauer [47] and Hilado et al. [49] measured the time to death of mice exposed to the pyrolysis products from a series of nylon-containing fabrics decomposed by ramp heating the materials at 40°C/min without any forced airflow. The maximum animal exposure time was 30 minutes. The calculated mean times to death from replicate tests ranged from 19.97 ± 0.40 minutes for a 28% nylon/72% rayon fabric to 8.93 ± 1.06 minutes for a 14% nylon/86% wool fabric (Table 25). For reference purposes, the mean time to death was 11.91 minutes for a 100% cotton fabric and was either 12.40 minutes

or 18.61 minutes for a 100% rayon fabric depending on the type of rayon. Calculated mean times to death of animals exposed to the decomposition products from several 100% nylon fabrics ranged from 18.52 minutes to 19.10 minutes.

Hilado et al. [50] reported mean times to death and incapacitation for another series of nylon blended fabrics and one nylon plastic (nonfibrous) material (Table 26). These values are consistent with the other reported values. The nonfibrous nylon produced results comparable to that from the 100% nylon material reported in Table 25. The presence of wool appears to greatly reduce the time to death and time to incapacitation.

4.4 NBS TOXICITY PROTOCOL

The National Bureau of Standards (NBS) toxicity protocol has been described in detail by Levin et al. [66] and Kaplan et al. [34]. The sample is introduced into a cup furnace set at 25°C above or below the sample's auto-ignition temperature. It is a static system in that all of the combustion products are contained in an exposure chamber that provides for the head-only exposures of six male rats. The exposure lasts for 30 minutes at which time the animals are withdrawn and survivors held for 14 days of observation. Sample mass is varied in order to determine an LC₅₀ value based on the amount of material loaded in the furnace divided by the volume of the exposure chamber (200 l). Grand et al. [64] found that a nylon carpet with polypropylene primary and secondary backing in the flaming mode at 460°C had

a 30 minute LC_{50} value of 73.2 mg/l. The LC_{50} values of the non-flaming tests were indeterminable because of an insufficient number of fatalities.

A modification to the NBS Toxicity Protocol that replaced the cup furnace with a pair of radiant quartz heaters has been developed by Weyerhaeuser Co. [67]. This furnace arrangement was capable of delivering up to 75 kW/m² to the surface of a sample. Grand et al. [64] used this modified NBS Toxicity Protocol to determine LC_{50} values for three nylon carpet samples at two different energy levels. For non-flaming tests, the radiant heaters were set to deliver 25 kW/m² to the sample surface, while flaming tests involved exposing the sample to an initial incident energy level of 50 kW/m² for 10 minutes followed by 20 minutes of exposure at 25 kW/m². One of the carpet samples (82-11-1-1) was evaluated under both non-flaming and flaming conditions. In the non-flaming mode, the 30 minute LC_{50} value was 76.6 mg/l and the LA_{50} value was 69.4 cm². The flaming mode resulted in a 30 minute LC_{50} of 52.4 mg/l and an LA_{50} value of 47.5 cm². Two additional carpet samples were evaluated in the flaming mode. One sample, CT3-1, was tested with and without an underlayment. The carpet/underlayment combination had a 30 minute LC_{50} value of 45.5 mg/l while the carpet, alone, had a 30 minute LC_{50} value of 56.2 mg/l. Carpet sample CT3-2 with a rubberized hair pad had a 30 minute LC_{50} value ranging from 60 mg/l to 73 mg/l. The 30 minute LC_{50} results for the flaming mode are summarized below.

| <u>Sample</u> | <u>Underlayment</u> | <u>LC₅₀ (mg/l)</u> |
|---------------|---------------------|-----------------------------------|
| 82-11-1-1 | No | 52.4 |
| CT3-1 | No | 56.2 |
| CT3-1 | Yes | 45.5 |
| CT3-2 | Yes | 60-73 |

Grand et al. believed that the predominant toxic effects were caused by CO and HCN which were generated in sufficient quantities to produce the observed toxicities.

4.5 MISCELLANEOUS

Cornish [51] developed two different combustion systems to evaluate the toxicities of the combustion products from a series of materials. The first test method consisted of a static system in which the whole bodies of 15 rats were placed in a 1500 liter stainless steel exposure chamber along with a combustion tube furnace. A sample was inserted into the combustion tube furnace and heated to 700°C for 6 to 10 minutes. The second system contained a flow-through combustion tube furnace connected to a Pyrex cylinder which allowed 5 rats to be exposed in a nose-only mode. In the flow-through system, the temperature was increased at either 3°C/min or 5°C/min to a maximum of 800°C with a 1.0 l/min airflow in the furnace. The combustion effluent was mixed with 1.0 l/min laboratory air prior to entering the animal exposure chamber. A 4 hour exposure was used in the static system, while in the dynamic system, the animals were exposed to the combustion gases for 140

minutes. Cornish [51] and Cornish et al. [52] found that nylon had an LL₅₀ (exposure plus 7 days) of 33 g to 47 g (LC₅₀ of 22 to 33 mg/l) in the static system and 2.7 g to 4.3 g (LC₅₀ of 9 to 15 mg/l) in the dynamic system (Table 27). No correlation seems to exist between the dynamic and static exposures.

Using the static system, Cornish et al. [52] compared rat and rabbit responses to the combustion products generated by degradation of 20 g of a flame retarded and non-flame retarded nylon 6,6. They found that no rats died due to either exposure, but 1 out of 4 rabbits died following exposure to the non-fire retarded nylon 6,6. The degradation products of the flame retarded nylon 6,6 produced no rabbit deaths.

Cornish et al. [53] conducted a detailed blood analysis of rats exposed to a flame retarded nylon 6,6. Animals were exposed to either non-flaming (415°C) or flaming (800°C) combustion products from 35 g of nylon 6,6 decomposed in the static system. They measured plasma thiocyanate levels and found that, under non-flaming conditions, exposed animals had an average concentration of 54 $\mu\text{mol}/\text{ml}$ of thiocyanate as compared to 60 $\mu\text{mol}/\text{ml}$ detected in a control group. Under flaming conditions, the exposed group had 249 $\mu\text{mol}/\text{ml}$ of thiocyanate, while the control group had 67 $\mu\text{mol}/\text{ml}$. In addition, they found in the static system that 30 g or less produced no deaths but that 50 g or more produced 100% mortality under flaming decomposition conditions. Comparable values for the dynamic system were 2.5 g for 0% mortality and 5.0 g for 100% mortality.

MacFarland and Leong [54] designed a 300 liter steel box that contained 12 individual animal baskets and a set of three cone heaters. Flaming combustion was initiated by using a match ignited by one heater, while non-flaming combustion was initiated and sustained by use of all three heaters. Twelve rats were exposed in the whole body mode for 60 minutes. Survivors were kept for two weeks of observation. They reported the results of tests conducted with polyurethane foam and a nylon material coated with polyurethane such that 30% of the total mass was urethane and 70% was nylon. Non-flaming data were reported as $L(Ct)_{50}$ values and were 2100 $\text{mg} \cdot \text{min/l}$ and 1900 $\text{mg} \cdot \text{min/l}$ for polyurethane foam and polyurethane/nylon, respectively. Histological examinations showed that flaming combustion was less toxic than non-flaming combustion. In the case of non-flaming polyurethane, death was attributed to acute asphyxia resulting from occlusion of the upper respiratory tract. Pulmonary edema appeared to be the cause of death from the non-flaming polyurethane/nylon.

Kishitani and Nakamura [55,56] exposed the whole bodies of individual mice to the combustion products generated by heating the test polymer in a quartz-glass tube and monitored animal activity during the exposure. The quartz-glass tube was heated by a set of gas burners to one of three temperatures - 350, 500, or 750°C. A natural draft of about 4 l/min caused the smoke to flow from the combustion system to the exposure system. The exposure system was a 56 liter glass chamber containing a wire cage with a vibration sensor installed in the cage floor. The time that animals died was determined from the vibration sensor. Surviving animals were observed for a post-exposure period of one week. The concentrations of CO and HCN were

measured continuously and HCl was sampled periodically. Smoke density was also recorded continuously. Exposures lasted 15 minutes. Table 28 tabulates the results of burning nylon 6,6 rods in air. No deaths were recorded during the exposures conducted at 350 or 500°C. At 750°C, animals died in 2.92 to 3.67 minutes, CO levels were approximately 0.23% and HCN was 417 ppm. Since more CO was generated at the lower temperatures where no deaths occurred, these deaths cannot be attributed to CO alone. The high concentration of HCN generated at the higher temperature added to CO is more likely the cause of these deaths.

Kishitani and Yusa [57] developed an empirical relationship between sample weight of material and the time a set of mice in freely revolving cages would collapse. Their apparatus consisted of a combustion system similar to that of Kishitani and Nakamura [55], but exposed 5 mice at a time rather than one. The animals were in individual free-wheeling cages within a 55 liter glass chamber. The maximum exposure time was 15 minutes. During this period, they monitored the number of revolutions of each animal cage. In experiments where nylon 6,6 rods were decomposed at 550 and 850°C, they found that the equation

$$W = kT^p$$

where

W = weight of sample (g)

T = collapse time (min)

k, p = computed constants

was a reasonable representation of the data within the range of 2.5 to 3.5 minutes (Table 29). At 550°C, k was found to be 1.48 and p was -1.09, while at 850°C, k was 0.68 and p was -1.11.

Wright and Adams [58] investigated the toxicity of the combustion products from a series of polymeric materials. They used two 54 liter polytetrafluoroethylene-coated stainless steel chambers, one for a combustion chamber and the other for an exposure chamber. In the combustion chamber, samples were heated by a hot plate for a maximum of 5 minutes and by an acetylene/air burner 8 cm above the sample surface for 30 seconds. The atmosphere was moved between the two chambers at 200 ℓ/min . Six animals were exposed per test in a whole body mode for 5 minutes. Nylon, under these conditions was found to have an LL_{50} of 6.8 g or an LC_{50} of 61.9 mg/ ℓ . Under the same conditions, red oak had an LL_{50} of 11.40 or an LC_{50} g of 103.6 mg/ ℓ .

5.0 LARGE-SCALE TESTS

Several researchers have conducted large scale fire testing of furnishings and finishing materials containing nylon components. These investigators monitored the production of a number of gaseous combustion products in order to analytically quantify the toxicity of the combustion atmosphere. In general, nylon was tested in combination with other materials. It thus becomes very difficult to assess the toxic contribution of one material as compared to another since the overall toxicity is a result of the total

combustion products. However, comparisons between tests that differ in only one or two components can be made.

Hafer and Yuill [59] and Yuill [60] conducted a series of room fire tests that were designed to measure the fire performance of an innerspring mattress with various combinations of mattress pads, blankets, and pillows. In a second series of tests, the mattress was replaced by a chair upholstered with different fabrics in each test. The mattress tests were initiated by a dropped match, while the chair tests were started with a dropped cigarette. Carbon monoxide, CO₂, and O₂ concentrations were monitored. In all the tests, the innerspring mattress had a rayon ticking and was covered with a cotton sheet. The effect of changing the mattress pad from a cotton/nylon one to a cotton/rayon one was examined. Very little difference was noted between the two match ignition tests (Table 30). The maximum CO and CO₂ concentrations and minimum O₂ concentration as measured at the 5 foot level in the test chamber (12 ft x 14 ft x 8 ft) along with the time of occurrence of the maximum CO level are tabulated in Table 30. The upholstered chairs consisted of wood frames with urethane foam cushions. One of the chairs was covered with a nylon upholstery fabric which, when tested, appeared to yield similar results in comparison to other materials studied. The acetate covered chair produced the highest peak concentration of CO; on the other hand, the nylon and polypropylene covered chairs caused the lowest oxygen values.

Birky et al. [61] reported on large-scale floor covering tests conducted at the National Bureau of Standards. In these tests, a burn room and 30 foot

corridor were covered with various floor coverings. In two tests, nylon carpets were evaluated. The concentration of CO, CO₂, and O₂ were continuously monitored and samples of the combustion atmosphere were taken in evacuated bulbs for later analysis on a gas chromatograph and/or infrared spectrophotometer. The results showed that while CO and CO₂ values were relatively constant throughout the two tests, large quantities of HCN were generated after the corridor had undergone flashover (Table 31).

Alderson and Breden [62] utilized the same facility to evaluate the importance of a carpet underlayment in fire growth. In all tests, they used a nylon carpet as the primary floor covering and varied the padding material below the carpet. Four wood cribs (total of 170 lbs) were placed in the burn room for use as an energy source to induce flame spread on the carpeting. A carpet runner was extended from the burn room into the corridor. The section of carpeting in the burn room ignited 180 to 240 seconds into the test.

Table 32 summarizes the results of these tests. In those tests resulting in flashover, large quantities of HCN only appeared in post-flashover gas samples. Although flames spread along the carpet runner and into the corridor, no HCN was detected in those tests that did not achieve flashover. The maximum HCN concentration (8000 ppm) and CO concentration (5.5%) occurred with a urethane pad below the nylon carpet.

Grand et al. [64] conducted a series of furnished large-scale fire tests in a burn room/corridor/target room configuration. The overall test design consisted of a 12 ft x 18 ft burn room perpendicular to the closed end of a 45 ft corridor, with an 8 ft x 12 ft target room located 16 feet from

the burn room. Of the four tests performed in this facility, two tests included carpeting (sample # CT3-2; also discussed in section 4.4) and an underlayment. The burn room was furnished to duplicate a "typical" hotel room and included a dresser, desk, desk chair, table, two upholstered chairs, a sofa, two night stands, and a queen size bed with all bedding. In addition to analytical measurements of temperature, gases (CO, CO₂, O₂, HCN, and HCl), and smoke density, rats were exposed in a head-only position to the combustion products collected in the target room.

Two groups of animals were used in each test. One group of seven animals was exposed to the combustion products beginning with the initiation of the fire test, while a second group of five animals were inserted into the target room wall when the target room door was closed. Time to death was noted for each exposure group.

Each test began with the smoldering ignition of an upholstered chair that was in contact with the sofa. Smoldering combustion continued until the chair burst into flames. Fire growth continued until flashover occurred (tests 2,3,4). In tests 3 and 4, the carpet became involved prior to flash-over. The door to the target room was open 1 inch at the start of tests 2,3,4 and 12 inches for test 1. Five minutes after a thermocouple at the 7 ft level in the burn room indicated 1200°F, the target room door was closed. Table 33 summarizes the maximum or minimum gas values for the burn room and target room as well as the mean time to death for each group of animals. With the exception of test one, which began with a larger target room door opening, the presence or absence of carpeting had little effect on the mean

time to death of either group of animals. Although test one shows shorter times to death, the values of the measured gases in the target room were not significantly different from the other tests with the exception of the minimum oxygen and maximum HCN concentrations. Grand et al. noted that HCl or HCN were not detected until flaming was noted in the burn room.

6.0 CONCLUSIONS

Typical pyrolysis products from a broad range of nylons do not appear to differ greatly in their nature. Many of the decomposition products detected in vacuum pyrolysis experiments appear as products of thermal degradation in inert and air atmospheres. There is a general reduction in the quantities of heavier hydrocarbons and an increase in the production of CO and CO₂ as the temperature or the oxygen content of the atmosphere are increased. The predominant gaseous products of decomposition in an air atmosphere were identified as: CO, CO₂, H₂O, NH₃, HCN, and NO_x. Many other volatile products were identified and are tabulated in this review.

The toxicity of the thermal degradation products from various types of nylon have been evaluated by nine different protocols. Reported LC₅₀ values ranged from 10.75 mg/l [41] to 61.9 mg/l [58]. This variation is attributed to differences in nylon formulations used by various researchers as well as variations in test protocols. Dyes [45,46,47] apparently did not affect the material's combustion product toxicity as indicated by the exposure time necessary to cause death, but an increase in the amount of backcoating [47,48] on a nylon fabric decreased the time needed to produce death. Time

to death measurements showed that the volatile products from nylon are less toxic than those from rayon or cotton, while the blending of wood to nylon greatly increased the toxicity of the thermal decomposition products. In general, however, the overall toxicity of the thermal degradation products from nylon do not appear to be greatly different than those from many other polymeric materials.

As expected, the role of nylon in the reported large-scale tests was ambiguous and difficult to interpret since the nylon was a single component in a multicomponent system. Two large-scale test programs indicated that the generation of HCN in toxicologically significant quantities was limited to post-flashover conditions [61,62]. A third set of tests [64] also showed that the presence of flaming conditions was required to produce HCN.

7.0 ACKNOWLEDGEMENTS

The authors gratefully acknowledge the help of N. Jason, M. Diephaus, A. Durham, and C. S. Bailey, who performed the literature search and compiled the references.

This work was performed under Contract CPSC-IAG-74-25, Task Order 84.8 from the U. S. Consumer Product Safety Commission (CPSC), Dr. Rita Orzel, Project Officer. The opinions expressed herein are those of the authors and not those of CPSC.

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Table 1
Thermophysical Properties of Nylons

| <u>Property</u> | <u>Measured Value</u> | <u>Reference</u> |
|---------------------------|-----------------------|------------------|
| Melting point | 172-260°C | 2,9 |
| Heat of combustion | 31-33 MJ/kg | 10 |
| Activation energy | 180-223 kJ/mole | 6,7 |
| Ignition temperature | | |
| flash ignition | 421-590°C | 3,4,5,6,8 |
| self ignition | 424-532°C | 4,8 |
| Decomposition temperature | 310-380°C | 8 |
| Oxygen Index | 20.1-28.7 | 5,8 |

Table 2

Mass Spectrometric Analyses of Gaseous Fractions From
the Pyrolysis of Polyamide Copolymers [12]

| <u>Product</u> | Weight % of <u>original specimen</u> | |
|-----------------|---|-------------------|
| | <u>Nylon 6</u> | <u>Nylon 6,10</u> |
| Carbon monoxide | 0.11 | 0.00 |
| Carbon dioxide | 3.50 | 4.56 |
| Hydrocarbons | 0.40 | 0.18 |
| Cyclopentanone | 1.38 | 0.05 |
| Water | 1.67 | <0.10 |

Table 3

Hydrocarbons Detected in the Pyrolysate of
Polyamide Copolymers [12]

| <u>Product</u> | <u>Nylon 6</u> | <u>Nylon 6,10</u> |
|-----------------|----------------|-------------------|
| Benzene | + | - |
| Butane | + | + |
| Butene | + | + |
| Cyclohexene | + | - |
| Cyclopentadiene | + | + |
| Cyclopentanone | + | + |
| Ethane | + | + |
| Ethylene | + | + |
| n-Hexane | + | + |
| Methane | + | + |
| Pentadiene | + | + |
| Pentane | + | + |
| Pentene | + | + |
| Propane | + | + |
| Propene | + | + |

+ = detected

- = not detected

Table 4

Mass Spectrometric Analysis of Volatile Fractions from
the Pyrolysis of Various Polyamides [13]

| Compounds | Mixture | Nylon 6, m.w. ^a | | Nylon 6,10 (Mol %) |
|---------------------------------------|--------------------|----------------------------|---------|--------------------------|
| | Nylon | 30,000 | 60,000 | |
| | 6 & 6,6 (Mol %) | (Mol %) | (Mol %) | |
| CO ₂ | 43.7 | 55.8 | 59.4 | 64.3 |
| H ₂ O | 47.8 | 35.4 | 35.6 | 16.3 |
| Ethylene | 0.4 | 0.4 | 0.3 | -- |
| Ethane | 0.3 | -- | 0.2 | -- |
| Propadiene | -- | -- | 0.1 | -- |
| Propylene | 0.5 | 0.4 | 0.7 | -- |
| Propane | 0.2 | -- | -- | -- |
| Butadiene | -- | 0.2 | 0.4 | -- |
| Butene | 0.2 | 0.2 | 0.6 | -- |
| Butane | 0.1 | 0.3 | 0.5 | -- |
| Isoprene | -- | 0.3 | 0.2 | -- |
| Cyclopentene | 0.1 | -- | -- | -- |
| Cyclopentanone | 5.8 | -- | -- | -- |
| Pentadiene | 0.1 | -- | -- | -- |
| Pentene | 0.2 | 0.1 | 0.3 | -- |
| Pentane | -- | 0.1 | 0.1 | -- |
| Benzene | 0.4 | 5.8 | 0.1 | 13.3 |
| Cyclohexene | 0.1 | -- | -- | -- |
| Hexadiene | 0.1 | 0.3 | 0.7 | 6.1 |
| Hexene | -- | 0.4 | 0.2 | -- |
| Hexane | -- | 0.1 | 0.2 | -- |
| Toluene | -- | 0.1 | 0.1 | -- |
| Dimethylbenzene | -- | -- | 0.1 | -- |
| Heptadiene | -- | 0.1 | 0.2 | -- |
| Total | 100.0 | 100.0 | 100.0 | 100.0 |
| Fraction of pyrolyzed material (%) | 5 | 5 | 10 | 1 to 2 |

^a - molecular weight

Table 5

 Pyrolysis Products of Four Polyamides
 Determined by Gas Chromatography/Mass Spectrometry [17]

| Temp. (°C) | Compound | Peak Area (%) | | | |
|---------------|---------------------------|---------------|---------|---------|----------|
| | | nylon 6 | nylon 7 | nylon 8 | nylon 11 |
| 510 | Hydrocarbons ^a | 2.5 | 8.2 | 2.7 | 25.8 |
| | Cyclopentanone | - | 6.5 | - | - |
| | C ₁₁ -nitrile | - | - | - | 14.0 |
| | Caprolactam | 94.9 | - | 13.4 | 18.0 |
| | C ₇ -lactam | - | 62.0 | - | - |
| | C ₈ -lactam | - | - | 68.3 | 11.2 |
| | C ₁₁ -lactam | - | - | - | 13.1 |
| | Others | 2.6 | 23.3 | 15.6 | 17.9 |
| | Residue (% by weight) | 75 | 25 | 80 | 80 |
| 610 | Hydrocarbons ^a | 33.5 | 28.6 | 45.2 | 31.9 |
| | Benzene | - | 3.8 | 1.6 | 2.2 |
| | Acrylonitrile | - | - | 1.8 | 2.4 |
| | Acetonitrile | - | 3.8 | 2.9 | 2.6 |
| | Pyrrolidine | - | - | 1.8 | - |
| | Cyclopentanone | - | 9.1 | 2.9 | 2.3 |
| | Cyclohexanone | - | 3.3 | 0.9 | 0.9 |
| | C ₁₁ -nitrile | - | - | - | 9.3 |
| | Caprolactam | 62.8 | - | 5.6 | 4.4 |
| | C ₇ -lactam | - | 17.6 | - | - |
| | C ₈ -lactam | - | - | 18.0 | 2.4 |
| | C ₁₁ -lactam | - | - | - | 5.9 |
| | Others | 3.7 | 33.8 | 19.3 | 35.8 |
| | Residue (% by weight) | 50 | 0 | 80 | 70 |
| 770 | Hydrocarbons ^a | 30.9 | 40.8 | 34.2 | 17.6 |
| | Benzene | - | 14.7 | 1.2 | 1.4 |
| | Acrylonitrile | - | - | 2.1 | 2.4 |
| | Acetonitrile | 4.6 | 3.6 | 4.3 | 8.9 |
| | Pyrrolidine | - | 1.3 | 1.4 | 1.9 |
| | Cyclopentanone | - | 4.6 | 1.4 | 9.0 |
| | Pyridine | - | 2.1 | - | - |
| | Cyclohexanone | - | 5.1 | 0.9 | 1.8 |
| | C ₁₁ -nitrile | - | - | - | 2.7 |
| | Caprolactam | 59.2 | 2.6 | 12.3 | 7.7 |
| | C ₇ -lactam | - | 4.8 | - | - |
| | C ₈ -lactam | - | - | 12.3 | 2.1 |
| | Others | 5.3 | 19.1 | 28.5 | 41.5 |
| | Residue (% by weight) | 0 | 0 | 60 | 70 |

^a - Hydrocarbons with five carbons or less

Table 6

Thermooxidation Products of Four Polyamides Determined by
Gas Chromatography/Mass Spectrometry [17]

| <u>Identified Substance</u> | <u>Peak Area %</u> | | | |
|-------------------------------|--------------------|----------------|----------------|-----------------|
| | <u>Nylon 6</u> | <u>Nylon 7</u> | <u>Nylon 8</u> | <u>Nylon 11</u> |
| Butane + butene | 9.3 | - | 4.0 | 0.5 |
| Diazomethane + diazoethane | - | 2.3 | - | - |
| Butadiene | - | - | - | 0.3 |
| Methylbutane + methylbutylene | - | - | 4.1 | - |
| Pentene-1 | 8.0 | 6.1 | 0.3 | 0.7 |
| Pentane | - | - | 0.5 | 1.4 |
| Cyclopentadiene | 2.0 | - | - | - |
| Methylbutadiene | - | 1.2 | 0.5 | - |
| Pentadiene | 0.7 | - | - | - |
| Cyclopentene | 5.3 | - | - | - |
| Hexene | - | 6.0 | - | 3.7 |
| Hexane | - | 0.3 | 0.4 | - |
| Methylcyclopentene | - | 0.3 | 0.1 | - |
| Hexadiene | - | 0.6 | 0.2 | - |
| Trichloromethane | - | - | - | 19.8 |
| Methylcyclopentane | - | 0.5 | - | - |
| Benzene + n-methylpyridine | 9.5 | - | - | - |
| Cyclohexene | - | 1.2 | 0.9 | - |
| Heptene | - | 0.2 | 0.3 | 1.9 |
| Heptane | - | - | 0.6 | 0.8 |
| Heptadiene | - | 0.3 | 0.2 | 0.2 |
| Cyclopentanone | 17.8 | - | - | - |
| Toluene | - | 4.1 | 1.4 | 0.1 |
| Octene-pyridine | - | 4.3 | - | - |
| Octane | - | 1.5 | 0.9 | 2.3 |
| Hexenaldoxime-octadiene | - | 0.9 | - | - |
| Dimethylcyclohexene | - | - | 2.9 | - |
| Hexanitrile | - | - | 2.9 | - |
| 3-nonadiene | - | - | - | 1.8 |
| Cyclohexanonoxime | - | 1.2 | - | - |
| Nonene | - | - | - | 3.4 |
| Cyclohexanone | 29.0 | 3.5 | - | - |
| Nonane | - | - | - | 1.2 |
| Methylcyclohexanone | - | 3.5 | - | - |
| Octatriene | - | 6.2 | 0.5 | - |
| Adiponitrile | - | - | 3.5 | - |
| Decadiene | - | - | - | 0.9 |
| Decene | - | - | - | 3.5 |
| Cyanobenzene | - | 1.8 | 0.3 | - |
| Dimethylpyridine | - | 1.3 | - | - |
| Pimelonitrile | - | - | 27 | - |

Table 6 (continued)

| <u>Identified Substance</u> | Peak Area % | | | |
|------------------------------------|----------------|----------------|----------------|-----------------|
| | <u>Nylon 6</u> | <u>Nylon 7</u> | <u>Nylon 8</u> | <u>Nylon 11</u> |
| Nonenylcyanide | - | - | - | 4.5 |
| Phenol | - | 1.1 | - | - |
| Cresol | - | 2.0 | - | - |
| Undecene + undecane | - | - | - | 1.4 |
| Indoline + caprylic acid | - | - | 1.8 | - |
| Nonenylcyanide + nornonenylcyanide | - | - | - | 3.8 |
| Phenylbutane | - | 2.0 | - | - |
| Decylnitrile | - | - | 1.4 | - |
| C ₅ -Benzene | - | - | 1.4 | - |
| Caprolactam | 1.2 | 23.1 | 2.8 | 1.5 |
| Undecadennitrile + undecenitrile | - | - | 1.0 | - |
| Methylcaprolactam | - | - | 1.0 | - |
| Not identified | 17.2 | 24.5 | 43.7 | 6.3 |

Table 7

Combustion Products of Nylons Decomposed in
Different Oxygen Concentrations [18]

| <u>Compound</u> | Compound concentration when decomposed in | |
|-----------------|--|--------------------------------|
| | 20.9% O ₂ (mg/g) | 11.7% O ₂ (mg/g) |
| CO ₂ | 1226.0 | 907.0 |
| CO | 304.0 | 355.0 |
| Formaldehyde | 6.4 | 6.5 |
| HCN and RCN | 7.6 | 9.8 |
| NH ₃ | 32.0 | 210.0 |

Table 8

Combustion Products Generated by Decomposing Nylon 6 and
Nylon 6,6 by TGA in Air at 370°C [19,20]

| <u>Compound</u> | Compound concentration | |
|---|--------------------------------|----------------------------------|
| | Nylon 6 (mg/g) ^a | Nylon 6,6 (mg/g) ^b |
| H ₂ O | 18.40 | 15.70 |
| CO | - | 0.86 |
| CO ₂ | 4.86 | 9.19 |
| NH ₃ | 0.17 | 0.83 |
| C ₂ and C ₃ species | 0.01 | 0.03 |
| C ₄ - C ₁₀ | - | 0.07 |
| C ₅ species | TR | TR |
| Benzene | 0.01 | 0.02 |
| Toluene | TR | 0.01 |
| C ₂ -benzene | - | TR |
| Methanol | - | 0.03 |
| Ethanol | - | TR |
| C ₄ -Alcohols | - | TR |
| Acetaldehyde | TR | TR |
| C ₄ -Acetaldehyde | - | TR |
| C ₅ -Acetaldehyde | - | TR |
| Acetone | - | TR |
| 2-Hexanone | - | TR |
| 3-Heptanone | | 0.02 |
| Cyclopentanone | 0.01 | 0.48 |
| 3-Methylcyclopentanone | - | 0.05 |
| Cycloheptanone | - | 0.02 |
| Dimethyloxymethane | - | TR |
| p-Dioxane | - | 0.02 |
| 2-Methyl-1,3-dioxane | - | 0.01 |
| Ammonium carbonate | - | 26.20 |
| Pyridine | - | 0.07 |
| 2-Methylpyridine | - | 0.02 |
| Residue (%) | 89.5 | 73.3 |

TR: trace amounts < 0.01 mg/g

a: reference 19

b: reference 20

Table 9

**Analysis of Cup Furnace Flaming Decomposition
of Nylon 6,6 in Air at Two
Airflow Rates [21]**

| <u>Compound</u> | <u>Concentration at airflow rate of:</u> | |
|-------------------------------|--|---------------------------------|
| | <u>50 l/h</u> <u>(mg/g)</u> | <u>100 l/h</u> <u>(mg/g)</u> |
| CO ₂ | 563 | 590 |
| CO | 194 | 205 |
| C ₂ H ₄ | 82 | 94 |
| CH ₄ | 39 | 40 |
| HCN | 26 | 31 |
| C ₂ H ₂ | 7 | 15 |
| NH ₃ | 4 | 10 |

Table 10

Production of HCN and CO During Flaming Degradation of
Nylon 6,6 in a Tube Furnace in an Air or
Nitrogen Atmosphere^a [24]

| Temperature (°C) | HCN | | CO | |
|---------------------|---------------|--------------------|---------------|--------------------|
| | Air (mg/g) | Nitrogen (mg/g) | Air (mg/g) | Nitrogen (mg/g) |
| 700 | - | 79 | - | 83 |
| 800 | 95 | 104 | 143 | 143 |
| 900 | 110 | 118 | 305 | 270 |
| 1000 | 116 | 105 | 436 | 310 |
| 1100 | 72 | 82 | 732 | 455 |

a - Flow rate was 50 ml/min

Table 11

Production of NO₂ From the Thermal Degradation of Nylon 6,6^a [25]

| <u>Temperature</u> (°C) | <u>NO₂</u> (mg/g) |
|----------------------------|---------------------------------|
| 600 | 8.4 |
| 700 | 4.0 |
| 800 | 2.3 |
| 900 | 5.7 |
| 1000 | 9.4 |

a - Experimental conditions: Tube furnace, airflow of 500 ml/min.

Table 12

Concentrations of Selected Products from the
Thermal Decomposition of Nylon 6 in Air [27]

| Temperature (°C) | CO (mg/g) | CO ₂ (mg/g) | HCN (mg/g) |
|---------------------|--------------|---------------------------|---------------|
| 500 | 64 | 190 | 52 |
| 600 | 79 | 232 | 65 |
| 700 | 71 | 195 | 79 |
| 800 | 76 | 142 | 95 |

Table 13

HCN Production From the Thermal Degradation of
Three Nylons in Nitrogen or Air Atmospheres [30]

| <u>Nylon Designation</u> | <u>Temperature (°C)</u> | <u>HCN Concentrations in</u> | |
|------------------------------|-----------------------------|------------------------------|--------------------|
| | | <u>Nitrogen (%)</u> | <u>Air (%)</u> |
| 6,6 | 600 | 0.08 | 0.15 |
| | 800 | 1.55 | 1.74 |
| | 1000 | 6.95 | 6.83 |
| | 1200 | 10.03 | 8.86 |
| 11 | 600 | 0.02 | 0.08 |
| | 800 | 0.43 | 0.81 |
| | 1000 | 2.42 | 2.68 |
| | 1200 | 10.25 | 10.27 |
| 12 | 600 | 0.01 | 0.02 |
| | 800 | 0.56 | 0.98 |
| | 1000 | 4.06 | 3.84 |
| | 1200 | 6.06 | 3.73 |

Table 14

Concentrations of Specific Combustion Products Found During
NBS Smoke Chamber Tests of Materials Containing Nylon [31]

| Sample Number | Sample Weight (g) | Description | Exposure | | | Gas Concentration (ppm/g) ^a |
|---------------|-------------------|--|----------|-----------------|--------|--|
| | | | CO | HC ₂ | Others | |
| 3 | 2.8 | Modacrylic/nylon/cotton fabric | F | 80 | 40 | 15 |
| 4 | 2.6 | Nylon fabric | N | 20 | 25 | 10 |
| 23 | 50.0 | Molded nylon | F | 30 | 0 | 0 |
| 53 | 5.9 | Filled rubber on nylon 6,6 fabric backed by glass fiber batt. | F | 230 | 15 | 10 |
| 54 | 4.1 | Organic filled nylon fabric w/glass fiber batt. | N | 90 | 8 | 5 |
| 55 | 0.9 | Polyethylene film over nylon fabric (filled rubber) | F | 140 | 8 | 6 |
| 56 | 0.6 | Organic filled nylon 6,6 | N | 80 | 1 | 7 |
| 58 | 2.6 | Modacrylic/nylon/cotton fabric | F | 160 | 50 | 2 |
| 75 | 3.9 | Cotton/nylon-trace polyester | N | 80 | 35 | 1 |
| 138 | 1.0 | Nylon/cotton-50/50 | F | 120 | 9 | 3 |
| 156 | 1.3 | PVF on nylon fabric | N | 50 | 5 | 1 |
| | | | | 20 | 40 | 15 |
| | | | | 25 | 25 | 10 |
| | | | | 180 | 0 | 5 |
| | | | | 120 | 0 | 5 |
| | | | | 100 | 0 | 4 |
| | | | | 40 | 0 | 2 |
| | | | | 100 | 0 | 0 |
| | | | | 40 | 0 | 0 |
| | | | | | HF=35 | |
| | | | | | HF=24 | |

F = Flaming exposure

N = Non-flaming exposure

PVF = Poly(vinyl flouride)

a = Gas concentration per unit mass of material

Table 15

Comparison of Colorimetric Detector Tubes and Instrumental Methods for Analyzing Gases Generated from the Thermal Decomposition of Two Flame Retarded 90% Wool, 10% Nylon Upholstery Fabrics in the NBS Smoke Chamber [32]

| Sample # | Analysis Method | Gas Concentration (mg/g) | | | | | | |
|----------|-----------------|--------------------------|-----|------|------------------|-----|------|-----------------|
| | | CO | HCl | HCN | H ₂ S | HBr | HCHO | SO ₂ |
| 70 | CDT | 48.7 | 0 | 8.2 | 11.8 | - | 0 | 33.4 |
| | IMA | 48.0 | 0 | 12.1 | 18.8 | T | 0.3 | 6.2 |
| 142 | CDT | 74.3 | 0 | 12.9 | 10.8 | - | 0 | 10.2 |
| | IMA | 69.0 | 0 | 9.2 | 15.5 | T | 0.4 | 3.2 |

CDT = Colorimetric detector tubes

IMA = Instrumental methods of analysis

T = Trace

Table 16

Comparison of Combustion Products Generated in a Combustion Tube Furnace
From Two Flame Retarded 90% Wool, 10% Nylon Upholstery Fabrics [32]

| <u>Sample #</u> | Gas Concentration (mg/g) | | | | | | | |
|-----------------|--------------------------|-----|------|------------------|-----|------|-----------------|-----------------|
| | CO | HCL | HCN | H ₂ S | HBr | HCHO | SO ₂ | NO ₂ |
| 70 | 78.2 | 0 | 33.8 | 13.9 | 0 | 0.8 | 0 | 0 |
| 142 | 112.0 | 0 | 37.2 | 14.2 | 0 | 0 | 1.5 | 0 |

Table 17

Thermal Decomposition of Three Nylon Carpet Samples in an Infrared Pyrolysis Instrument [33]

| <u>Sample Description</u> | <u>Gas Concentrations^a</u> | | | | | |
|--|---------------------------------------|-------------------------------------|---------------------------|---------------------------|-----------------------------|---------------------------|
| | <u>O₂</u> <u>(%)</u> | <u>CO₂</u> <u>(%)</u> | <u>CO</u> <u>(ppm)</u> | <u>HC</u> <u>(ppm)</u> | <u>HCHO</u> <u>(ppm)</u> | <u>HCℓ</u> <u>(mg)</u> |
| 40% nylon 11; 60% PVC w/dioctyl phthalate | 11.8 | 7.4 | 17500 | 9380 | 167 | 31513 |
| 35% nylon 6,6; 65% jute w/paper | 16.8 | 3.1 | 12400 | 20400 | 197 | - |
| 25% nylon 6; 75% polyisoprene | 16.4 | 4.0 | 2800 | 15500 | 154 | - |

a - Results are normalized to one square foot of carpet per cubic meter of air

Table 18

Summary of Toxicity Protocols

| No. | Protocol Name | Animal species | Exposure time (min) | Endpoint | Animal exposure | | Combustion system | | Combustion flow system | |
|-----|---------------------------|----------------|---------------------|-------------------------------|----------------------------------|---------------------------|---------------------------|----------------------|------------------------|--------|
| | | | | | WB ^b /NO ^c | tube furnace | tube furnace | recirculated | vented | vented |
| 1 | *DIN | rats | 30 | 1. incapacitation 2. death | WB | tube furnace | tube furnace | recirculated | vented | |
| 2 | *FAAA ^a | rats | 30 | 1. incapacitation 2. death | WB | tube furnace | tube furnace | recirculated | vented | |
| 3 | *NASA/USF | mice | 30 | 1. incapacitation 2. death | WB | tube furnace | tube furnace | vented/non-vented | vented | |
| 4 | *NBS | rats | 30 | 1. incapacitation 2. death | HD ^d | cup furnace | cup furnace | non-vented | non-vented | |
| 5 | Cornish A B | rats rats | 240 140 | death death | WB NO | tube furnace | tube furnace | non-vented vented | non-vented vented | |
| 6 | MacFarland and Long | rats | 60 | death | WB | radiant heaters | radiant heaters | non-vented | non-vented | |
| 7 | Kishitani and Nakamura | mice | 15 | death | WB | gas tube furnace | gas tube furnace | vented | vented | |
| 8 | Kishitani and Yusa | mice | 15 | death | WB | gas tube furnace | gas tube furnace | vented | vented | |
| 9 | Wright and Adams | | 60 | death | WB | hot plate + open flame | hot plate + open flame | non-vented | non-vented | |

* = Described by Kaplan et al. [34]

a = Animals in an exercise wheel during exposure

bWB = Whole body exposure

cNO = Nose only exposure

dHD = Head exposure

Table 19

DIN Toxicity Test Results of a Treated and Non-treated
85% Wool, 15% Nylon Carpet with a Jute Backing [36]

| Sample | Temperature (°C) | Weight loss (%) | Maximum CO (ppm) | CO ₂ (%) | Mean O ₂ (%) | Min O ₂ (%) | Mean Respiration ^a (%) |
|-----------------|---------------------|--------------------|------------------------|------------------------|-------------------------------|------------------------------|---|
| Non- treated | 500 | 77 | 2040 | 0.8 | 20.3 | 19.0 | 57 |
| | 600* | 89 | 130 | 2.8 | 17.5 | 14.5 | 98 |
| | 700* | 86 | 410 | 3.2 | 17.7 | 16.5 | 117 |
| Treated | 500* | 75 | 5470 | 3.8 | 18.0 | 12.5 | 29 |
| | 600* | 88 | 1290 | 3.8 | 17.6 | 11.5 | 74 |
| | 700* | 95 | 1400 | 3.5 | 16.9 | 15.0 | 75 |

* = Flamed

^a = Percent of control value (pre-exposure)

Table 20

Description of Nylon Containing Materials Evaluated by
FAA Toxicity Test Method [37]

| <u>Sample Number</u> | <u>Thickness (mm)</u> | <u>Weight (kg/m²)</u> | <u>Description</u> | <u>Use</u> |
|----------------------|-----------------------|----------------------------------|---------------------------------------|-------------------|
| 142 | 0.89 | 0.38 | Flame retarded, 90% wool/10% nylon | upholstery fabric |
| 70 | 0.94 | 0.35 | Flame retarded, 90% wool/10% nylon | upholstery fabric |
| 89 | 1.50 | 0.89 | Flame retarded, PVC-nylon | fabric |

Table 21

Incapacitation and Lethality Results From Exposures to Thermal Degradation Products from Nylon-containing Materials Decomposed According to the FAA Protocol [37]

| Sample Number | Measured | | Normalized charged | | Normalized consumed | |
|---------------|----------------------|----------------------|----------------------|----------------------|----------------------|----------------------|
| | <u>T_i</u> | <u>T_d</u> | <u>T_i</u> | <u>T_d</u> | <u>T_i</u> | <u>T_d</u> |
| 142 | 2.85 | 6.04 | 2.22 | 4.70 | 2.01 | 4.26 |
| 70 | 3.66 | 8.27 | 2.72 | 6.16 | 2.36 | 5.36 |
| 89 | 14.29 | - | 10.70 | - | 9.89 | - |

T_i = Mean time to incapacitation

T_d = Mean time to death

- = No response during 30 minute exposure

Measured = Mean of observed values

Normalized charged = Measured values normalized to a standard 200 g animal and 1 g of material based on amount of material placed in furnace.

Normalized consumed = Same as normalized charged except based on amount of material consumed

Table 22

Effects of Acid Dyes on the Toxicity of a
Nylon 6,6 Fabric [45,46]

| <u>Type of Dye</u> | <u>Time to Death^a (min)</u> |
|--------------------|--|
| none | 25.40 \pm 0.59 |
| Green 25 | 25.53 \pm 2.87 |
| Green 40 | 24.82 \pm 1.82 |
| Red 151 | 25.36 \pm 1.36 |
| Yellow 38 | 24.72 \pm 0.65 |

^a mean and standard deviation

Table 23

Effects of Backcoating on the Toxicity of a
Nylon 6,6 Fabric [45,47,48]

| <u>Backcoating (%)</u> | <u>Time to Death (min)</u> |
|----------------------------|--------------------------------|
| 0 | 18.52 \pm 5.63 ^a |
| 26 | 16.70 \pm 0.06 |
| 32 | 23.75 \pm 7.43 |
| 35 | 16.34 \pm 3.50 |
| 37 | 13.48 \pm 0.72 |
| 43 | 12.82 \pm 0.94 |

^a Mean and standard deviation

Table 24

Effects of Various Heating Conditions on the Toxicity of the Pyrolysis Products from Upholstery Fabrics Containing Nylon [49]

| Method | Mean time to | | | |
|--------|----------------------|-----------------|------------------|------------------|
| | Incapacitation (min) | | Death (min) | |
| | nylon | wool/nylon | nylon | wool/nylon |
| B | 11.84 \pm 2.35 | 5.34 \pm 0.83 | 23.75 \pm 7.42 | 8.93 \pm 1.06 |
| F | 3.92 \pm 0.11 | 1.36 \pm 0.01 | 15.03 \pm 4.83 | 3.04 \pm 0.57 |
| G | 1.86 \pm 0.52 | 1.24 \pm 0.13 | 5.00 \pm 2.94 | 3.70 \pm 2.61 |
| H | 2.79 \pm 0.48 | 1.08 \pm 0.36 | 6.01 \pm 2.94 | 2.55 \pm 0.99 |
| E | 11.03 \pm 8.82 | 2.79 \pm 0.30 | 25.13 \pm 0.41 | 10.13 \pm 3.91 |
| I | 2.97 \pm 0.67 | 1.82 \pm 0.25 | 7.97 \pm 2.00 | 3.47 \pm 0.17 |
| J | 2.34 \pm 0.60 | 1.80 \pm 0.67 | 7.77 \pm 2.67 | 8.70 \pm 3.39 |

Method B = 40°C/min, 200°-800°C, no forced air flow

Method E = 600°C, fixed temperature, no forced air flow

Method F = 800°C, fixed temperature, no forced air flow

Method G = 800°C, fixed temperature, forced air flow 16 ml/s

Method H = 800°C, fixed temperature, forced air flow 48 ml/s

Method I = 600°C, fixed temperature, forced air flow 16 ml/s

Method J = 600°C, fixed temperature, forced air flow 48 ml/s

Material:

100% nylon (0.40 kg/m²) plus backcoating (0.13 kg/m²)

86% wool/14% nylon (0.43 kg/m²) plus backcoating (0.10 kg/m²)

Table 25

NASA/USF Toxicity Protocol B Results for a Series of Nylon Containing Fabrics [47]

| Sample Designation | Material Description | Time to death ^a (min) |
|--------------------|--|----------------------------------|
| 278-76 | 100% nylon | 18.52 + 5.63 |
| 291-76 | 100% nylon | 19.10 + 3.34 |
| 276-76 | 62% nylon, 38% rayon | 15.53 + 0.19 |
| 244-76 | 57% nylon, 43% rayon | 15.74 + 5.79 |
| 269-76 | 44% nylon, 56% rayon | 12.63 + 2.82 |
| 280-76 | 28% nylon, 72% rayon | 19.97 + 0.40 |
| 214-76 | 100% rayon | 12.40 + 0.15 |
| 248-76 | 100% rayon | 18.61 + 3.80 |
| 236-76 | 33% nylon, 49% rayon, 18% cotton | 13.28 + 1.71 |
| 274-76 | 30% nylon, 3% rayon, 67% cotton | 15.34 + 2.26 |
| 275-76 | 23% nylon, 41% rayon, 36% cotton | 12.91 + 1.90 |
| 213-76 | 10% nylon, 63% rayon, 27% cotton | 10.92 + 0.66 |
| 279-76 | 2% nylon, 70% rayon, 28% cotton | 19.43 + 2.62 |
| 648-75 | 100% cotton | 11.91 + 1.63 |
| 266-76 | 14% nylon, 37% rayon, 39% cotton, 10% acetate | 14.63 + 1.36 |
| 265-76 | 9% nylon, 57% rayon, 23% cotton, 11% acetate | 12.97 + 1.65 |
| 219-76 | 9% nylon, 43% rayon, 25% cotton, 25% acetate | 11.37 + 0.35 |
| 263-76 | 3% nylon, 11% rayon, 61% cotton, 25% acetate | 12.38 + 0.81 |
| 238-76 | 30% nylon, 41% rayon, 29% acetate | 14.63 + 4.57 |
| 457-76 | 15% nylon, 54% rayon, 24% cotton, 6% polyester | 14.12 + 2.60 |
| 245-76 | 14% nylon, 86% wool | 8.93 + 1.06 |
| NBS1975#1 | 12% nylon, 88% wool | 10.96 + 4.81 |

^a mean and standard deviation from replicate tests.

Table 26

Mean Times to Death and Incapacitation for Some
 Nylon Containing Materials Tested According to
 NASA/USF Toxicity Protocol B [50]

| Material | Time to death (min) | Time to incapacitation (min) |
|----------------------------|-------------------------------|---------------------------------|
| 100% nylon fabric | 16.78 \pm 3.49 ^a | 12.01 \pm 1.74 ^a |
| 85-90% nylon, wool fabric | 8.87 \pm 1.01 | 5.68 \pm 1.06 |
| 52-72% rayon, nylon fabric | 15.60 \pm 3.86 | 10.99 \pm 3.07 |
| 57-62% nylon, rayon fabric | 15.62 \pm 0.15 | 12.18 \pm 0.26 |
| 100% nylon (plastic) | 14.36 \pm 1.71 | 12.35 \pm 1.44 |

^a Mean and standard deviation

Table 27

Comparison of Dynamic and Static Exposures
for Nylon Materials [51,52]

| Material | Static LL ₅₀ (g) ^a | Dynamic LL ₅₀ (g) | Heating Rate (°C/min) |
|----------------|---|---------------------------------|--------------------------|
| nylon yarn | 47 | 4.3 | 3 |
| nylon fabric | 43 | 2.6 | 3 |
| nylon 6,6 | 37 | 2.7 | 5 |
| nylon 6,6 (FR) | 37 | 3.2 | 5 |
| nylon knit | 33 | 3.0 | 3 |

^a Amount of material loaded into the furnace necessary to cause 50% of the animals to die within 4 hour (static) or 140 minute (dynamic) exposure plus 7 day post-exposure observation period

FR = Flame retarded

Table 28

Results of Animal Exposures to the Combustion Products of Nylon 6,6 Decomposed at Three Different Temperatures [55,56]

| Heating temperature (°C) | Specimen weight (g) | Weight loss (g) | Time of death (min) | Maximum Concentration | | | |
|--------------------------|---------------------|-----------------|---------------------|-----------------------|---------|-----------|-------------|
| | | | | CO (%) | HCℓ (%) | HCN (ppm) | Smoke (m⁻¹) |
| 350 | 5.0 | 3.8 | L | 0.39 | ND | 43 | 22.8 |
| | | 3.7 | L | 0.32 | ND | 49 | 22.1 |
| | | 3.7 | L | 0.41 | ND | 42 | 22.8 |
| 500 | 1.0 | 1.0 | L | | | | |
| | | 1.0 | L | 0.07 | ND | 11 | 14.7 |
| | | 1.0 | L | | | | |
| 750 | 1.0 | 1.0 | 2.92 | | | | |
| | | 1.0 | 3.67 | 0.23 | ND | 417 | 3.9 |
| | | 1.0 | 3.50 | | | | |

L = animal survived exposure

ND = none detected

Table 29

Results of Animal Exposures to Nylon 6,6 Decomposition Products Produced at 550°C and 850°C [57]

| Temperature (°C) | Sample weight (g) | Collapse time ^a (min) |
|---------------------|----------------------|-------------------------------------|
| 550 | 0.39 | 2.63 \pm 1.29 |
| | 0.45 | 3.02 \pm 0.35 |
| | 0.71 | 1.96 \pm 0.26 |
| | 1.01 | 1.48 \pm 0.08 |
| 850 | 0.15 | 3.51 \pm 0.36 |
| | 0.24 | 2.64 \pm 0.60 |
| | 0.36 | 1.86 \pm 0.47 |
| | 0.58 | 1.19 \pm 0.17 |

^a = Mean and standard deviation

Table 30

Gas Analysis of Large-Scale Tests of
Innerspring Mattresses and Upholstered Chairs [59,60]

| Test number | Furnishing item | Additional material | Ignition mode | Gas concentrations ^c | | | Time max CO (min) |
|-------------|-----------------------|----------------------|---------------|---------------------------------|-------------------------|------------------------|-------------------|
| | | | | Max CO (ppm) | Max CO ₂ (%) | Min O ₂ (%) | |
| 17 | mattress ^a | cotton/nylon pad | match | 5300 | 3.8 | 17.7 | 63.0 |
| 16 | mattress | cotton/rayon pad | match | 6200 | 3.5 | 17.7 | 49.5 |
| 23 | chair ^b | rayon fabric | cigarette | 1130 | 1.7 | 17.6 | 162.0 |
| 24 | chair | cotton fabric | cigarette | 1950 | 4.2 | 17.6 | 94.5 |
| 26 | chair | nylon fabric | cigarette | 1800 | 5.0 | 15.9 | 166.5 |
| 27 | chair | acetate fabric | cigarette | 3750 | 4.1 | 17.0 | 170.3 |
| 28 | chair | polypropylene fabric | cigarette | 2900 | 4.8 | 15.4 | 116.3 |

^a innerspring mattresses with rayon ticking and cotton sheet.^b upholstered chair with wood frame and urethane foam cushions^c gases were measured at the 5 foot level in the center of the testroom (12 x 14 x 8 ft.)

Table 31

Large-Scale Nylon Carpet Tests Using
NBS Corridor Facilities [61]

| Test Number | Distance from floor (ft) | Time of Sampling (sec) | Flashover Time (sec) | | CO ₂ (%) | CH ₄ (%) | C ₂ H ₄ (%) | C ₂ H ₂ (%) | HCN (ppm) |
|-------------|--------------------------|------------------------|----------------------|-----------------|---------------------|---------------------|-----------------------------------|-----------------------------------|-----------|
| | | | CO | CH ₄ | | | | | |
| 342 | 8 | 285 | 300 | 2 | 15 | 0.2 | 0.3 | 0.06 | 100 |
| | 8 | 308 | | 3 | 16 | 0.3 | 0.7 | 0.05 | 200 |
| | 7 | 322 | | 3 | 18 | 0.4 | 0.2 | 0.10 | 100 |
| | 4 | 338 | | 5 | 16 | 1.4 | 0.6 | 0.50 | 600 |
| | | | | | | | | | |
| 348 | 8 | 450 | 440 | 5 | 15 | 1.5 | 0.6 | 0.60 | trace |
| | 8 | 570 | | 4 | 18 | 0.8 | 0.3 | 0.40 | 2,000 |
| | 7 | 585 | | 4 | 18 | 0.4 | 0.3 | 0.10 | 3,000 |
| | 4 | 605 | | 3 | 14 | 0.2 | 0.2 | 0.10 | 500 |

Table 32

Results of Gas Analysis for Large-Scale Tests of
Nylon Carpet and Various Underlayment [62]

| Test Number | Underlayment | Flashover time (sec) | Maximum Gas Concentrations | | | |
|-------------|--------------------|----------------------|----------------------------|---------------------|---------------------|-----------------------------------|
| | | | CO (%) | CO ₂ (%) | CH ₄ (%) | C ₂ H ₄ (%) |
| 355 | wood cribs alone | NF (600) | 1.5 | 10.2 | 0 | 0 |
| 356 | carpet alone | NF (600) | 1.2 | 11.5 | 0 | 0 |
| 357 | hair jute | NF (300) | 3.0 | 14.5 | 0.7 | 0.1 |
| 358 | virgin urethane | NF (600) | 0.5 | 3.6 | 0 | 0 |
| 361 | rebonded urethane | 810 | 5.0 | 18.3 | 1.3 | 3.5 |
| 362 | test 361 plus glue | 600 | 5.2 | 19.2 | 1.4 | 0.7 |
| 363 | test 358 plus glue | 720 | 5.5 | 17.8 | 1.4 | 0.7 |
| 364 | latex | 690 | 4.5 | 17.0 | 0.8 | 0.3 |
| 365 | virgin urethane | 630 | 5.2 | 18.0 | 1.8 | 1.0 |
| 367 | integral SBR | 690 | 4.0 | 17.0 | 0.8 | 0.2 |
| 368 | hair jute | 810 | 4.5 | 14.5 | 1.0 | 0.7 |

NF = no flashover; values in () are time of maximum CO
 SBR = styrene butydiene rubber

Table 33

Results of Large-Scale Tests of a Fully Furnished Burn Room
Connected to a Corridor and Target Room [65]

| Test No. | Room | Gas Concentrations | | | | Time of Flaming (min:sec) | Time of Initial Exposure (min:sec) | Mean Time to Death (min:sec) |
|-------------|---------------------|------------------------|-------------------------------------|------------------------------------|---------------------------|------------------------------------|--|---------------------------------------|
| | | CO ^a (%) | CO ₂ ^a (%) | O ₂ ^b (%) | HCN ^a (ppm) | | | |
| 1c | Burn | 6.95 | 12.0 | 0.4 | 330 | 470 | 18:39 | 0:00 |
| | Target ^d | 1.76 | 5.1 | 11.3 | 70 | 540 | | 27:33 |
| 2c | Burn | 6.76 | 10.0 | 0.2 | 1160 | 590 | 18:41 | 0:00 |
| | Target ^e | 1.22 | 6.4 | 15.9 | 130 | 460 | | 29:50 |
| 3f | Burn | 7.07 | 14.2 | 0.2 | 1160 | 1170 | 18:55 | 0:00 |
| | Target ^e | 1.13 | 2.6 | 14.5 | 140 | 430 | | 30:48 |
| 4f | Burn | 6.29 | 13.4 | 0.2 | 1520 | 280 | 19:01 | 0:00 |
| | Target ^e | 1.17 | 4.5 | 13.9 | 150 | 520 | | 34:37 |
| | | | | | | | 28:49 | 34:44 |

a Maximum concentration

b Minimum concentration

c No carpeting

d Began with a 12 inch target room door opening

e Began with a 1 inch target room door opening

f Nylon carpet with underlayment

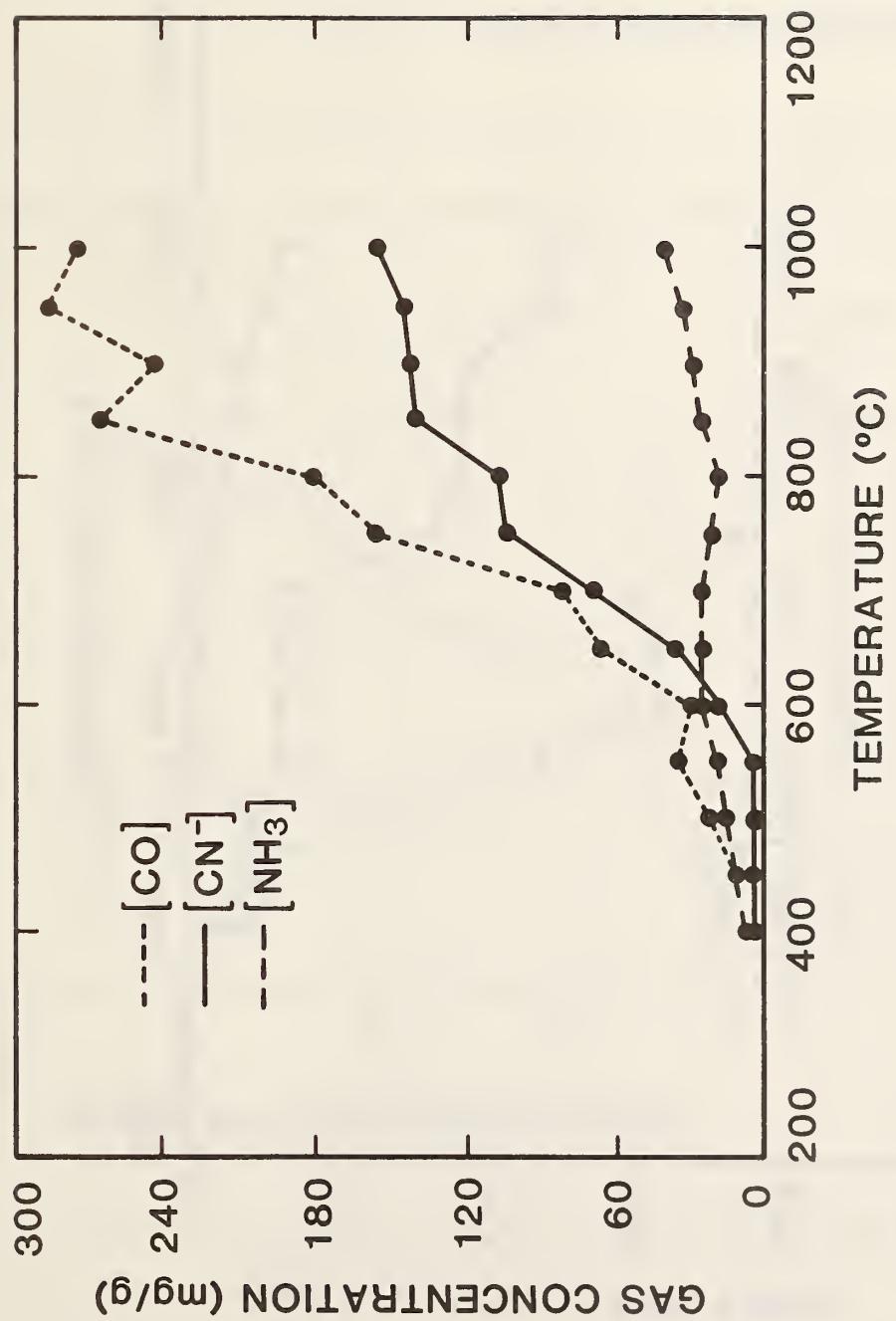


Figure 1. The Production of Specific Gases from the Decomposition of Nylon 6 in an Atmosphere of Nitrogen

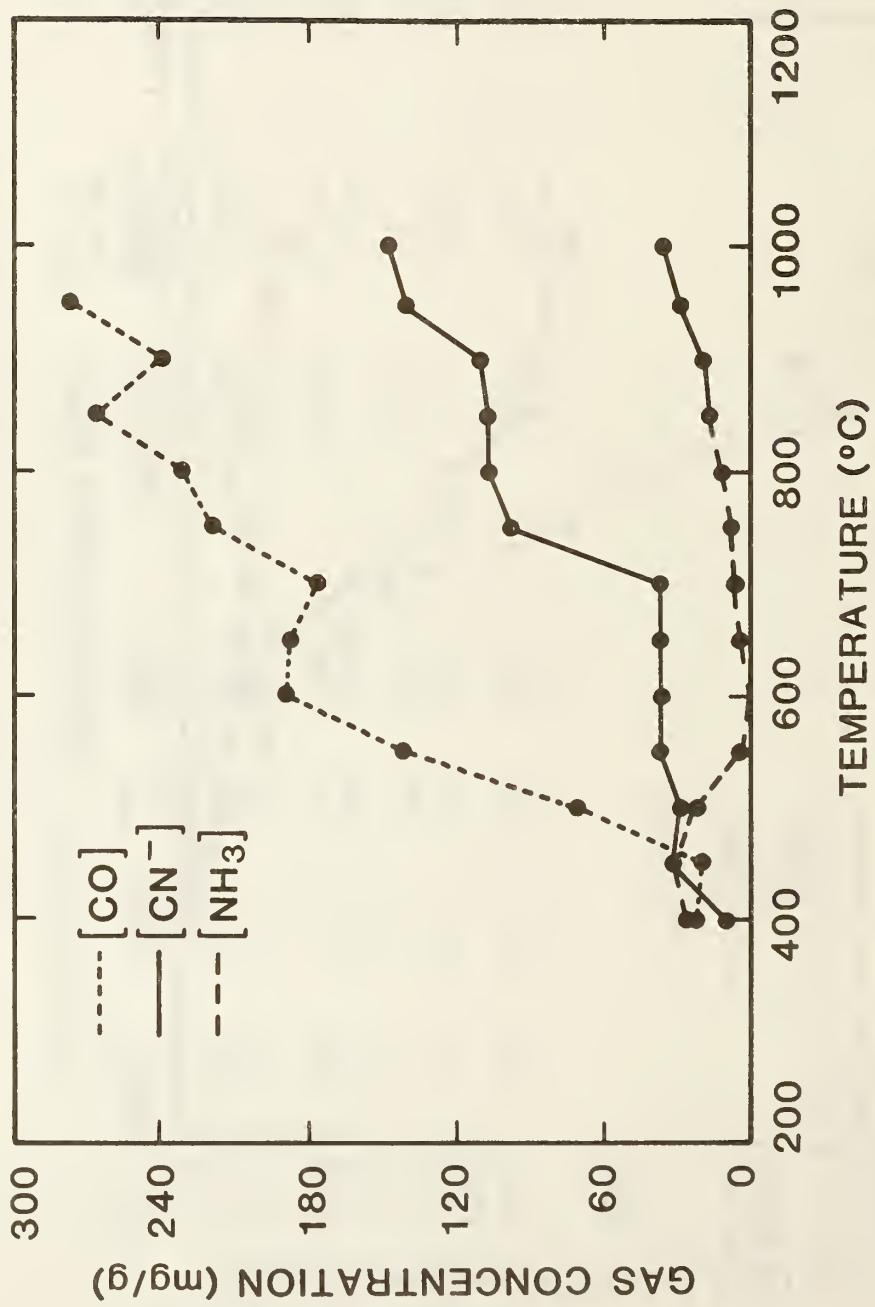


Figure 2. The Production of Specific Gases from the Decomposition of Nylon 6 in an Atmosphere of Air

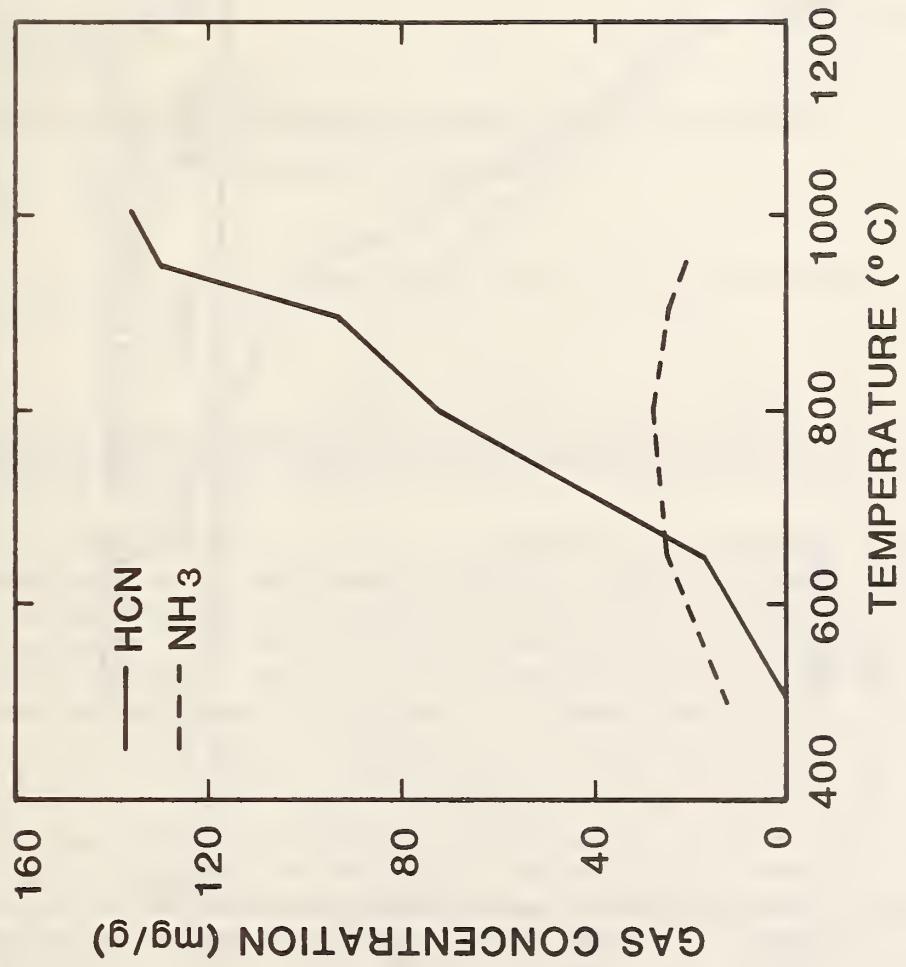


Figure 3. Comparison of HCN and NH₃ Production from the Decomposition of Nylon 6 in a Nitrogen Atmosphere

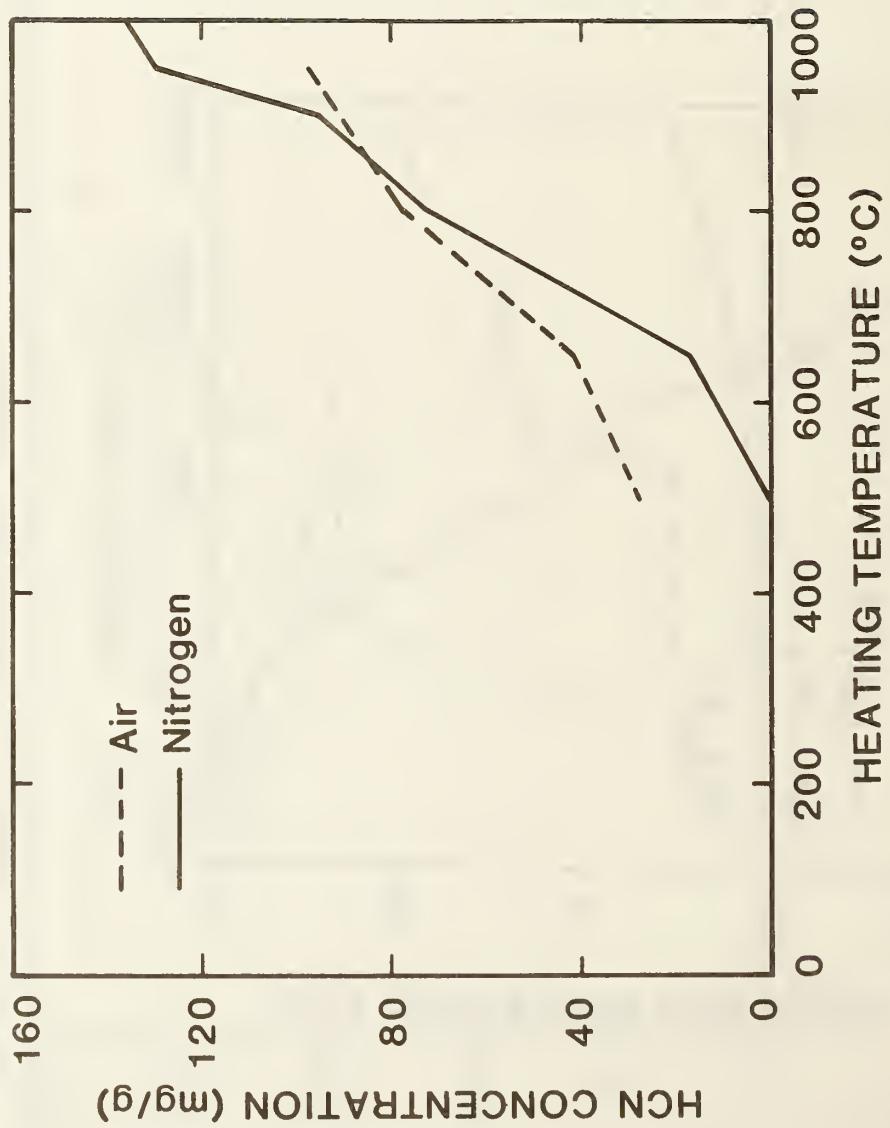


Figure 4. Production of HCN During Decomposition of Nylon 6

| | | | | |
|---|--|--|-----------------------------------|--------------------------------------|
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| 4. TITLE AND SUBTITLE NYLONS: A REVIEW OF THE LITERATURE ON PRODUCTS OF COMBUSTION AND TOXICITY | | | | |
| 5. AUTHOR(S) EMIL BRAUN AND BARBARA C. LEVIN | | | | |
| 6. PERFORMING ORGANIZATION (If joint or other than NBS, see instructions) NATIONAL BUREAU OF STANDARDS DEPARTMENT OF COMMERCE XWASHDC 20560, DCC X20230 Gaithersburg, MD 20899 | | | 7. Contract/Grant No. | 8. Type of Report & Period Covered |
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| 10. SUPPLEMENTARY NOTES <input type="checkbox"/> Document describes a computer program; SF-185, FIPS Software Summary, is attached. | | | | |
| 11. ABSTRACT (A 200-word or less factual summary of most significant information. If document includes a significant bibliography or literature survey, mention it here) The English literature through 1984 on polyamides was reviewed to determine the nature of the combustion products and their toxicity. This review was limited to aliphatic polyamides normally called nylon and excludes aromatic polyamides such as Nomex and bicomponent polymers. Typical pyrolysis products from a broad range of nylons do not appear to differ greatly. Many of the decomposition products detected in vacuum pyrolysis experiments appear as products of thermal degradation in inert and air atmospheres. In air, a general reduction in the quantities of heavier hydrocarbons is noted along with an increase in the production of CO, CO ₂ , H ₂ O, NH ₃ , HCN, and NO _x . The toxicity of the thermal degradation products from various types of nylon has been evaluated by nine different protocols. Reported LC ₅₀ values range from 10.8 mg/l to 61.9 mg/l. Dyes apparently do not affect the materials' combustion products toxicity, but an increase in the amount of backcoating on a nylon fabric increase toxicity. Time to death measurements show that volatile products from nylons are less toxic than those from rayons or cotton, while the blending of wool with nylon greatly increase the toxicity of the thermal decomposition products. In general, however, the overall toxicity of the thermal degradation products from nylon do not appear to be greatly different than those from many other polymeric materials. | | | | |
| 12. KEY WORDS (Six to twelve entries; alphabetical order; capitalize only proper names; and separate key words by semicolons) Combustion products; literature reviews; nylor; pyrolysis; thermal decomposition; toxicity | | | | |
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